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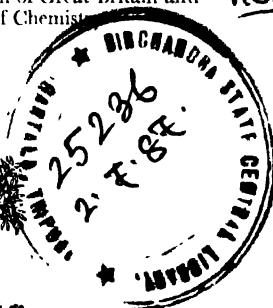C.H., O.B.E., M.C., F.R.S , M.A. (Cantab)

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PROFESSOR HAROLD ALBERT WILSON, M.A. D.Sc. F.R.S. *M.R.I.*

The Electrical Properties of Flame.

IF a flame is brought near to an insulated conductor charged with electricity, the charge disappears. This is explained by supposing that the gases in the flame are partially dissociated into ions. A neutral molecule splits up into two ions, one having a negative charge and the other a positive charge. The conductor, if positively charged, attracts the negative ions out of the flame, and their charges when they reach it neutralise its charge.

If a plate of an insulator, such as ebonite, is placed between the flame and the charged conductor, the ions are still attracted through the plate; but when they reach it they cannot get through, and so remain on its surface. The side of the plate turned towards the flame thus gets a charge of opposite sign to that on the conductor. This shows that the disappearance of the charge in the first case was due to an opposite charge attracted out of the flame, and not to the charge on the conductor escaping into the flame.

We have a stream of gas rising from the flame, and the ions go up in the stream. The ions of opposite sign attract one another, and when two come together their charges are neutralised and the two ions are said to have disappeared by recombination. Thus, as we go up in the stream of gas from the flame the number of ions diminishes. If the stream of gas is allowed to pass up a long tube containing along its axis a series of charged electrodes, then the bottom electrode will be discharged first, and then the next one, and so on. The ions are used up in discharging the electrodes, so that the electrodes are discharged in order, beginning with the lowest one. When the lower electrodes have been discharged, the upper ones begin to be discharged, but more slowly, because many of the ions disappear by recombination before they get far up the tube. Another effect also comes in; as the gases cool down the ions do not move so freely through them, and so are not so easily attracted by the electrodes. This makes the rate of discharge of the upper electrodes still slower.

Thus, as we go down towards the flame the number of ions and their mobility rapidly increases, and right inside the flame the number is so large that the flame behaves like a good conductor of electricity.

If the terminals of an induction coil are connected to two Bunsen

burners, sparks can be passed from the tip of one flame to the tip of the other. The temperature of the flame is about $2000°$ C., so that the density of the gases in it is about one-seventh of their density at the ordinary temperature. The potential difference required to send a spark through the flame is about the same as that required to send a spark through an equal length of air at one seventh of ordinary atmospheric pressure. It appears therefore that the ions do not make it easier for a spark to pass. This is due to the fact that the current in the spark is greater than the ions can carry, so that the potential difference has to be enough to produce more ions, and so is the same in the flame as in unionised air at the same density.

To study the conductivity of flame, it is convenient to use a row of small Bunsen flames placed so that they touch each other. I use a row of fifty flames burning from quartz tubes 1 cm. apart. This gives a flame 50 cm. long, and about 10 cm. high. The quartz tubes insulate very well, so that a current can be passed along the flame horizontally from one end to the other.

If two parallel platinum electrodes immersed in the flame are connected to a galvanometer and battery, it is found that a measurable current is obtained. The relation between the current (i) and the difference of potential (V) between the electrodes is given by the equation $V = Ai^2 + Bdi$ where A and B are constants and d denotes the distance between the electrodes. If d is small, say one or two millimetres, the term Bdi is negligible (except when i is very small), and we get $V = Ai^2$. In this case the current is almost independent of the distance between the electrodes.

The reason for this peculiar relation between the current and potential difference becomes apparent when the variation of the potential along the flame from one electrode to the other is examined. An electrometer is connected to two platinum wires, which are immersed in the flame and can be moved along horizontally between the electrodes. Each wire takes up the potential of the flame at the point where the wire is situated, so the deflection of the electrometer indicates the difference of potential between the two points where the wires are put in. Suppose one wire is allowed to touch the positive electrode and the other is gradually moved along the flame from the positive to the negative electrode. It is found that in the space between the electrodes there is a small uniform potential gradient, but near each electrode there is a comparatively sudden drop in the potential. The drop near the negative electrode is much larger than the drop near the positive electrode. Thus, nearly all the electromotive force of the battery is used up close to the negative electrode. This shows that nearly all the resistance offered by the flame to the passage of the current is close to the negative electrode. The positive ions in the flame move towards the negative electrode and the negative ions towards the positive electrode, in fact the current is carried through the flame by these two streams of ions. Hence, close to the

negative electrode the current must be carried entirely by positive ions moving towards it, and at the positive electrode the current must be entirely carried by negative ions. We find that the resistance near the negative electrode is much greater than near the positive electrode, so that we conclude that the negative ions carry the current more easily than the positive ions. With a given electric force, the negative ions move very much faster than the positive ions. It has been shown experimentally that the velocity of the negative ions is about 10,000 cm. per sec. for one volt per cm., while that of the positive ions is about 100 times smaller than this.

In the flame away from the electrodes the electric force is found to be proportional to the current, so that here the flame obeys Ohm's law like a metallic conductor. Its conductivity is about $10''$ times less than that of copper. In the equation $V = Ai^2 + Bdi$, the term Bdi is the part of the E.M.F. used up between the electrodes, so it is proportional to the current and to the distance. Professor Sir J. J. Thomson has shown theoretically that the drop of potential near the electrodes should be proportional to the square of the current, as is found experimentally to be the case.

The conductivity of a Bunsen flame may be compared with the conductivity of liquids, such as water. In pure water some of the molecules are dissociated into ions and the water is a conductor, although only a poor one. But if a salt like sodium chloride is dissolved in the water the salt dissociates into ions almost completely, and the conductivity is greatly increased. Suppose we hold a bead of salt on a platinum wire in a flame, then the salt volatilises and the flame is filled with its vapour, and, just as with the water, the conductivity is enormously increased.

With the long flame and an electrode at each end, we can try the effect on the current of putting salt in different parts of the flame between the electrodes. In this way it is easy to show that the current is practically unchanged, unless the salt vapour is put in close to the negative electrode, but in that case it produces a very great increase in the current. This confirms the conclusion that nearly all the resistance to the passage of the current is situated close to the negative electrode. When the salt is put in anywhere it diminishes the resistance there to a small fraction of its value, but it is only close to the negative electrode that the diminution in the total resistance is appreciable. If we measure the potential difference between two points in the flame away from the electrodes, and then put salt vapour in the flame between them, we find that the P.D. drops to a small fraction of its value although the current is the same as before. This shows clearly that the salt vapour greatly increases the conductivity wherever it is put in.

If some salt is put on the negative electrode, the sudden drop in potential there almost disappears, and we get a nearly uniform potential gradient from one electrode to the other, so that now the resist-

ance is nearly uniformly distributed along the flame. If now salt
vapour is put in anywhere between the electrodes the current is
increased. If, for example, we fill half the length of the flame with
salt vapour, we nearly double the current.

When salt is put on one electrode, the flame can be used as a
rectifier for an alternating current, for when the salted electrode is
negative the resistance of the flame is much smaller than when it is
positive.

I have measured the conductivities of a number of alkali salt
vapours in a current of air flowing along a platinum tube heated in
a gas furnace. An electrode was fixed along the axis of the tube,
and the current from it through the salt vapour to the surrounding
tube was measured with a galvanometer. It was found that at tem-
peratures above $1400°$ C., and with electro-motive forces of about
1000 volts, the current was proportional to the amount of salt passing
through the tube, and for different salts in equal quantities inversely
proportional to the electrochemical equivalent of the salt. This shows
that the quantity of electricity per molecule of salt is the same for all
salts. It was also found that the quantity of electricity carried per
molecule was equal to that carried per molecule when a solution of salt
in water is electrolysed. It appears therefore that the laws of electro-
lysis discovered by Faraday for liquids apply also to salts in the state
of vapour.

When a molecule of salt like sodium chloride dissociates into two
ions in water, the sodium atom forms the positive ion and the chlorine
atom the negative ion, and when a current is passed through the
solution the sodium is attracted to the negative electrode and the
chlorine goes to the positive electrode. We might expect the same
thing to happen when a current is passed through the salt vapour in
a flame. If we put two wires in the flame, and put some sodium salt
on one and then connect them to an induction coil, and pass a dis-
charge from the salted one to the other, we find that the yellow sodium
vapour appears at it when it is the negative pole but not when it is
positive. This shows that in the flame the positive ions of the salt
vapour contain the metal just as they do in solutions. The negative
ions, however, do not appear to be the same in flames as in solutions.
In flames the very high velocity of the negative ions indicates that
they are the electrons whose properties have been investigated in
vacuum tubes by Sir William Crookes and Sir Joseph Thomson.
The positive ion, then, is an atom or molecule, while the negative ion
is an electron, the mass of which is several thousand times smaller.
This is the explanation of the fact that the negative ions move 100
times more quickly than the positive ions.

[H.A.W.]

Friday, February 26, 1909.

SIR WILLIAM CROOKES, D.Sc. F.R.S., Honorary Secretary and
Vice-President, in the Chair.

PROFESSOR H. L. CALLENDAR, M.A. LL.D. F.R.S.

Osmotic Phenomena and their Modern Physical Interpretation.

OSMOTIC pressure is a phenomenon of such importance in the theory
of solutions, and in the interpretation of all vital processes, and so
much valuable work has recently been directed to its elucidation,
that, although it is a somewhat thorny and difficult subject, no
apology is needed for any serious attempt, however inadequate, at its
explanation. .

One of the earliest recorded experiments on osmotic pressure is
that of the Abbé Nollet, who found that a bladder containing alcohol,
when immersed in water, absorbed water so greedily as in many cases
to burst the bladder. The experiment illustrates in an imperfect
manner the fundamental property of all animal and vegetable mem-
branes of allowing some substances to pass through them by osmosis
more easily than others. In many cases such membranes, while freely
permeable to water, are practically impermeable to certain substances
in solution, and play the part of sieves in directing and controlling
diffusion. It will readily be understood that results of the greatest
importance to biology have been obtained by studying this property
of *semipermeability*, as it is called, but the application of natural
membranes to the physical study of the subject is necessarily limited
on account of the difficulty of obtaining sufficiently large and perfect
membranes capable of withstanding any considerable pressure.

Artificial membranes of sufficient fineness to be impermeable to
such substances as sugar in solution, were first prepared by Traube by
means of precipitated pellicles of substances like copper-ferrocyanide.
The first quantitative measurements of osmotic pressures of consider-
able magnitude were made by Pfeffer with membranes of this kind
deposited in the pores of earthenware pots fitted with suitable mano-
meters for indicating the pressure developed. Pfeffer found that
when a semipermeable vessel, filled with sugar solution, was immersed
in water, the membrane being freely permeable to water, but not to
the dissolved sugar, the solution absorbed water through the mem-
brane by osmosis until the internal pressure reached a certain magni-
tude sufficient to balance the tendency to absorption. The osmotic

pressure developed in the state of equilibrium was found to be proportional to the strength of the solution, and to increase with rise of temperature at the same rate as the pressure of a gas at constant volume. A few years later van 't Hoff, reviewing these experiments in the light of thermodynamics, showed that the osmotic pressure of a dilute solution should be the same as the pressure exerted by a number of molecules of gas equal to those of the dissolved substance in a space equal to the volume of the solution, that it should be the same for all solutions of equal molecular strength, and that osmotic pressure followed the well-known laws of gas-pressure in all respects. The most important generalisation was hailed as the first step to a complete kinetic theory of solution, and the osmotic pressure itself has generally been regarded as due to the bombardment of the sides of the semipermeable membrane by the particles of solute, as though they were able to move freely through the solution with velocities comparable to those of the molecules of a gas. Such a view would not now be seriously maintained, but the fascinating simplicity of the gas-pressure analogy has frequently led to the attempt to express everything in terms of the osmotic pressure, regarded simply, but inaccurately, as obeying the gaseous laws, and has done much to divert attention from other aspects of the phenomena, which, in reality, are more important and have the advantage of being more easily studied. It was very soon discovered that the gaseous laws for osmotic pressure must be restricted to very dilute solutions, and that the form of the laws was merely a consequence of the state of extreme dilution, and did not necessarily involve any physical identity between osmotic pressure and gas-pressure. Many different lines of argument might be cited to illustrate this point, but it will be sufficient to take some of the more recent experimental measurements of osmotic pressure by the direct method of the semipermeable membrane.

Morse and Frazer in 1905 succeeded in preparing ferrocyanide membranes impermeable to sugar, and capable of withstanding pressures of more than 20 atmospheres. They operated by Pfeffer's original method, allowing water to diffuse into the solution in a porous pot until the maximum pressure was developed. There are many serious experimental and manipulative difficulties which the authors carefully considered and discussed in applying this method, but they succeeded in obtaining very consistent results. As a first deduction from their investigations they considered that they had established the relation that the osmotic pressure of cane-sugar was the same as that exerted by the same number of molecules of gas at the same temperature in the volume occupied by the solvent, and not in the volume occupied by the solution. In other words, the osmotic pressure of a strong solution was greater than that given by van 't Hoff's formula for a dilute solution in proportion as the volume of the whole solution exceeded the volume of the solvent contained in it. It was a very natural extension of the gas-pressure analogy to

deduct the volume occupied by the sugar molecules themselves in order to arrive at the space in which they were free to move. Unfortunately the later and more accurate series of measurements by the same experimentalists at 0° C. and 5° C., gave nearly the same osmotic pressures as at 24° C., and would appear to show, either that there is little or no increase of osmotic pressure with temperature, and that the pressures at 0° C. are much greater than those given by their extension of the gas-pressure analogy, or that one or other of the series of experiments are in error.

About the same time Lord Berkeley and E. J. Hartley undertook a series of measurements of the osmotic pressures of solutions of various kinds of sugar at 0° C. by a greatly improved experimental method, which permitted the range of pressure to be extended to upwards of 100 atmospheres. Instead of allowing the solvent to diffuse into the solution until the equilibrium pressure was reached, they applied pressure to the solution until balance was attained. The method of Lord Berkeley and Hartley possesses several obvious advantages, and it is impossible to study the original memoir without being convinced that they have really measured the actual equilibrium pressures with... order of certainty not previously attained or even approached. The pressures found were in all cases greatly in excess of those calculated from the gas-pressure of the sugar molecules in the volume occupied by the solution (according to van 't Hoff's formula for dilute solutions), or even in the restricted volume occupied by the solvent (according to Morse and Frazer's assumption).

Lord Berkeley endeavoured to represent these deviations on the gas-pressure analogy by employing a formula of the van der Waals type, with three disposable constants. Out of some fifty formulæ tested, the two most successful were those given in Table I. The constants A, a, and b were calculated to fit the three highest observations for each solution. Values calculated by the formulæ for the lower points were then compared with the observations at these points, with the results given in Table I. for cane-sugar. It is at once evident that, even with three constants, the gas-pressure analogy does not represent the results satisfactorily within the limits of error of experiment. Moreover, with three constants the equation cannot be interpreted, so that the gas-pressure analogy becomes useless as a working hypothesis, or as a guide to further research. On the vapour-pressure theory, to be next explained, the results are much better represented, as shown in column C, with but a single constant, and that a positive integer with a simple physical meaning.

VAPOUR-PRESSURE THEORY.

On the vapour-pressure theory, osmotic equilibrium depends on equality of vapour-pressure and not on an imaginary pressure which the particles of the dissolved substance would exert if they were in

Van 't Hoff	Morse and Frazer.	Lord B. (1).	Lord B. (2).	C.	Do. Observed. Lord B.
35·6	53·2	68·4	67·7	67·6	67·5
27·6	37·4	45·0	43·4	43·7	44·0
19·7	24·4	27·7	25·4	26·8	26·8
11·2	13·3	14·6	12·2	14·1	14·0

Lord Berkeley's equations—

$$(A/v - P + a/v^2)(v - b) = R T \quad . \quad . \quad . \quad (1)$$
$$(A/v + P - a/v^2)(v - b) = R T \quad . \quad . \quad . \quad (2)$$

the state of gas at the same volume and temperature. The vapour-pressure of any substance is a definite physical property of the substance which is always the same under the same conditions of pressure and temperature and state, and is easily measured in most cases for liquids and solutions. Equality of vapour-pressure is one of the most general, as well as the simplest, of all conditions of physical equilibrium. Ice and water can only exist together without change under atmospheric pressure at the freezing-point 0° C., at which their vapour-pressures are the same. Below the freezing-point the vapour-pressure of water is greater than that of ice. Either is capable of stable existence separately within certain limits, but if the two are put in communication, the vapour, being mobile, passes over from the water at higher pressure to the ice at lower pressure until equality of vapour-pressure is restored by change of temperature, or until the whole of the water is converted into ice.

In the case of ice and water, equality of vapour-pressure can also be restored by a suitable increase of pressure. This is the well-known phenomenon of the lowering of the freezing-point by pressure. By considering the equilibrium of water and vapour in a capillary tube, Lord Kelvin showed that the vapour-pressure of water, or any other liquid, was increased by pressure according to a very simple law, the ratio of the increase of vapour-pressure, dp, to the increase of pressure, dP, on the liquid being simply equal to the ratio of the densities of the vapour and liquid, or inversely as the specific volumes, v and V. This relation, which may be written $V dP = v dp$, is merely a special case of Carnot's principle, and was deduced by assuming the impossibility of perpetual motion. Assuming a similar relation to apply to ice, Poynting showed that when a mixture of ice and water was subjected to pressure, the vapour-pressure of the ice must be increased more than that of the water (since the specific

volume of ice is greater than that of water). Consequently, some of the ice must pass over into water, and the temperature must fall until the vapour-pressures are again equal. The lowering of the freezing-point by pressure, as observed by Lord Kelvin, and calculated by James Thomson, agrees precisely with that deduced as above from the condition of equality of vapour-pressure.

' ' Similar considerations apply to the equilibrium between a solution and the pure solvent, or between solutions of different strengths. To take a simple case, the vapour-pressure p'' of a sugar solution is always less than the vapour-pressure p' of water at the same temperature, and the ratio p''/p' of the vapour-pressures depends simply on the concentration of the solution, diminishing regularly with increase of concentration and being independent of the temperature. If separate vessels containing solution and water are placed in communication at the same temperature by a tube through which the vapour has free passage, vapour will immediately pass over from the water to the solution in consequence of the pressure difference, and will condense in the solution. The immediate effect is to produce equality of vapour-pressure by change of temperature. This takes only a few seconds. The vapour-pressure then remains practically uni: rm throughout. As diffusion proceeds and the temperature is slowly equalised, the water will gradually distil over into the solution, but the process of diffusion is so infinitely slow compared with the equalising of vapour-pressure that the final attainment of equilibrium would take years unless the solution were continually stirred.

The reason why equality of vapour-pressure is so important as a condition of physical equilibrium is that the vapour is so mobile and so energetic as a carrier of energy in the form of latent heat. The first effect is generally a change of temperature, but if the temperature is kept constant there must then be a change of concentration. Thus if two parts of the same solution are maintained at different constant temperatures, the concentrations will change so as to restore equality of vapour-pressure, if possible. Thus in a tube of solution, the two ends of which are maintained at different temperatures, the dissolved substance will appear to move towards the hotter end. What really happens is that the vapour, which is the mobile constituent, moves towards the colder end. If the tube is horizontal, with a free space above the liquid for the vapour, this transference will be effected with extreme rapidity. In fact, it will be practically impossible to establish an appreciable difference of temperature until the transfer is effected. If the vapour has to diffuse through the solution in a vertical column heated at the top, the process is greatly retarded, but the final effect is the same, and can be readily calculated from the relation between the vapour-pressure and the concentration.

In explaining the production of osmotic pressure as a necessary

consequence of the laws of vapour-pressure, there is one difficulty which, though seldom expressed, has undoubtedly served very greatly to retard progress. How can an insignificant difference of vapour-pressure, which may not amount to so much as one-thousandth part of an atmosphere in the case of a strong sugar solution at 0° C., be regarded as the cause of an osmotic pressure exceeding 100 atmospheres, or 100,000 times as great as itself ? The answer is that the equilibrium does not depend at all on the absolute magnitude of the vapour-pressure, but only on the work done for a given ratio of expansion, which is the same in the limit for a gramme-molecule of any vapour at the same temperature, however small the vapour-pressure. Indirectly the smallness of the vapour-pressure may have a great effect in retarding the attainment of equilibrium, especially if obstructive influences, such as other vapours or liquids, are present. Thus mercury at ordinary temperatures in the open air is regarded as practically non-volatile. Its vapour-pressure is less than a millionth of an atmosphere, and cannot be directly measured, though it may easily be calculated. When, however, we take mercury in a perfect vacuum, such as that of a Dewar vessel, the presence of the vapour is readily manifested by its rapid condensation on the application of liquid air in the form of a fine metallic mirror of frozen mercury. The least trace of air or other gas in the vacuum will retard the condensation excessively.

Under the conditions of an osmotic-pressure experiment we have solvent and solution in practical contact, separated only by a thin porous membrane. It will facilitate our conception of the conditions of equilibrium if we imagine the membrane to be a continuous partition pierced by a large number of very fine holes, of the order of a millionth of an inch in diameter. If the holes are not wetted by the solution or the water, the liquid cannot get through unless the pressure on it exceeds 100 atmospheres, but the vapour has free passage. If the solvent and solution are under the same hydrostatic pressure, the vapour-pressure of the solvent will be the greater, and the vapour will pass over into the solution. Since the surfaces are practically in contact, no appreciable difference of temperature can be maintained. If the solution is confined in a rigid envelope, so that its volume cannot increase, the capillary surfaces of the solution will rapidly bulge out as the vapour condenses on them, and the pressure on the solution will increase until condensation finally ceases, when the vapour-pressure of the solution is raised to equality with that of the pure solvent. The osmotic pressure is simply the mechanical pressure-difference which must be applied to the solution in order to increase its vapour-pressure to equality with that of the pure solvent. If any pressure in excess of this value is applied to the solution, the vapour will pass in the opposite direction, and solvent will be forced out of solution. The osmotic work required to force a gramme-molecule of the solvent out of the solu-

tion is the product of the osmotic pressure P by the change of volume U of the solution per gramme-molecule of solvent abstracted. In the state of equilibrium of vapour-pressure, this osmotic work P U must be equal to the work which the vapour could do by expanding from the vapour-pressure p' of the pure solvent to the vapour-pressure p'' of the solution. Neglecting minor corrections, we thus obtain the approximate relation—

$$P U = R \theta \log (p'/p'').^*$$

From this point of view the osmotic pressure of a solution is not a specific property of the solution in the same sense as the vapour-pressure, or the density, or the concentration, but is merely the mechanical pressure required under certain special conditions to produce equilibrium of vapour-pressure when neither the temperature nor the concentration are allowed to vary. One might with almost equal propriety speak of the "osmotic temperature" of a solution, meaning by that phrase the difference of temperature required to make the vapour-pressure of the solution equal to that of the pure solvent. The observation of the elevation of the boiling-point of a solution above that of the pure solvent is a familiar instance of a special case of such a temperature difference. It is just as much a specific property of the solution as the osmotic pressure, and would only require a perfectly non-conducting membrane for its production. No one would regard the rise of boiling-point as being the fundamental property of a solution in terms of which its other properties should be expressed. By similar reasoning osmotic pressure should not be regarded as existing *per se* in the solution, and as being the cause of the relative lowering of vapour-pressure and other phenomena. This point of view does not detract in any way from the reality and physical importance of the effects of osmotic pressure when it comes into play, but it puts the phenomena in their true light as consequences of the law of vapour-pressure.

Regarded as a verification of the laws of vapour-pressure, direct measurements of the osmotic pressure are of the highest value, but there are comparatively few cases known at present in which such direct measurements are possible. In other cases, the osmotic pressure, if it exists, can always be calculated from a knowledge of the vapour-pressure. For the elucidation of osmotic phenomena and many other problems in the theory of solutions, we are compelled to make a systematic study of the relations of vapour-pressure. Much has been done in this direction in the past, but, owing to the difficulty of the measurements, much remains yet to do. I may, therefore, be pardoned if I allude briefly to some of the methods

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* Obtained by integrating $U d P = v d p$. Plan k, Thermodynamik, also Zeit. Phys. Chem., xli. 212, 1902, and xlii. 584, 1903.

which I have employed for this purpose, and some of the conclusions at which I have so far arrived.

It is often a difficult matter, when the difference of vapour-pressure between a solution and the solvent is small, to measure the pressure difference directly to a sufficient degree of accuracy. A method very commonly employed, which has been brought to a high degree of accuracy by Lord Berkeley and his assistants, depends on the observation of the losses of weight of two vessels, containing solution and solvent respectively, when the same volume of air is aspirated slowly through them in succession. To secure accurate results, the air must pass very slowly. One complete observation takes about a week to perform successfully, and involves many difficult manipulations. I have endeavoured to avoid this difficulty by measuring the temperature difference in place of the pressure difference, since the temperature difference remains nearly constant, while the pressure difference tends to diminish in geometrical progression with fall of temperature. The method adopted for this purpose is that indicated in the diagram of the Vapour-Temperature Balance. The temperatures of solution and solvent, contained in separate vessels communicating through a tap, are adjusted, until, on opening communication between them, there is no flow of vapour from one to the other, as indicated by a change in the reading of a pair of thermo-junctions immersed in the solvent respectively. The corresponding difference of temperature is observed, and since the vapour-pressures of the solvent are known, it is easy to calculate the required ratio or difference of the vapour-pressures of solvent and solution at the same temperature. When the vapour-pressures are very small, it may be difficult to observe the change of temperature on opening the tap, unless the apparatus is very carefully exhausted. A more delicate method in this case is to observe the direction and magnitude of the current of vapour from solution to solvent, or *vice versâ*, by means of the " Vapour-Current Indicator," illustrated in the companion diagram. This consists of a delicately suspended vane, the deflections of which are read by a mirror, and will readily indicate a difference of pressure less than the thousandth part of a millionth of an atmosphere.

The vapour-current indicator is so constructed that its deflections are very accurately proportional to the pressure difference, much more so in fact than any form of electric galvanometer. It can also be employed for direct measurements of small differences of vapour-pressure. The chief difficulty in this case is to ensure the absence of air or other disturbing factors. A method of avoiding this difficulty is to work at atmospheric pressure, and to measure the pressure difference between two vertical columns of air saturated with the vapours of the solvent and solution respectively.* The temperature

* I first showed this experiment ten years ago, in illustration of the delicacy of the apparatus, at a Friday Evening Lecture at the Royal Institution.

difference may be adjusted to balance, and is preferably measured by means of a pair of differential platinum thermometers, which permits a higher order of accuracy to be attained than the thermo-electric method.

VAPOUR-PRESSURE IN RELATION TO MOLECULAR CONSTITUTION.

The well-known law of Raoult, according to which the relative lowering of vapour-pressure of a solution is equal to the ratio of the number of molecules n of the solute to the number of molecules of solvent N in the solution, has thrown a great deal of light on the molecular state of the dissolved substance in dilute solutions, but fails notably in many cases when applied to strong solutions. In the case of homogeneous mixtures of two indifferent volatile substances, such as benzol (C_6H_6) and ethylene chloride ($C_2H_4Cl_2$), which mix in all proportions without mutual action, a slightly different but equally simple law is known to hold very accurately throughout the whole range of concentration from 0 to 100 per cent. The vapour-pressure of each ingredient is simply proportional to its molecular concentration. In other words, the ratio of the partial vapour-pressure p' of either constituent at any concentration to its vapour-pressure p_0' in the pure state at the same temperature is equal to the ratio of the number of its molecules n' in the solution to the whole number of molecules $n' + n''$ of both substances in the solution. Such is evidently the form of the simple mixture law. For substances which form compounds in the solution, or whose molecules are associated or dissociated, this simple law is widely departed from. In a recent paper, "*On Vapour-Pressure and Osmotic Pressure of Strong Solutions*" (Proc. R.S.A., vol. lxxx. p. 466, 1908), I have endeavoured to extend this simple relation to more complicated cases by making the obvious assumption that, if compound molecules are formed, they should be counted as single molecules of a separate substance in considering their effect on the vapour-pressure. With this proviso the vapour-pressures of strong solutions are well represented by a natural extension of the simple mixture law, and it becomes possible to investigate the nature of the compounds formed in any case. To take a simple instance, suppose that each of the n molecules of the dissolved substance combines with a molecules of the solvent, the total number of molecules of the solvent being N. The ratio of the vapour pressure p'' of the solvent in the solution to the vapour-pressure p' of the pure solvent at the same temperature will then be the same as the ratio of the number $N - an$ of molecules of *free* solvent in the solution to the whole number of molecules $N - an + n$ in the solution, each compound molecule being counted as a single molecule.

With the simple formula—

$$p'/p'' = (N - an + n) / (N - an)$$

the values of the vapour-pressure are very easily calculated from the molecular concentration n for simple integral values of the hydration factor a. The osmotic pressures are also readily deduced from the ratio of the vapour-pressures (p'/p'') by the formula

$$P U = R T \log (p'/p'').$$

The value $a = 5$ fits the osmotic pressures for cane-sugar very well, as shown in the column headed C in Table I. The value $a = 2$ fits Lord Berkeley's observations on dextrose equally well up to pressures of 130 atmospheres. The same value $a = 5$ for cane-sugar also fits the observations on the depression of the freezing-point and the rise of the boiling-point, as it necessarily must, since these phenomena also depend on the vapour-pressure. The freezing-point method is the easiest for getting the ratio of the vapour-pressures to compare with the formula. At the freezing-point of an aqueous solution, the vapour-pressure of the solution must be the same as that of ice, provided that ice separates on freezing in the pure state. The ratio of the vapour-pressure of ice to that of water at any temperature below $0°$ C. is easily calculated. All the best recorded results, except those of a few associating substances, give simple positive integral values of a. Even in the case of associating substances, like Formic Acid and Acetone, the curves are of the same type, but the value of a is negative. Dissociating substances, like strong electrolytes, present greater difficulties, on account of the ionisation factor. But allowing for the uncertainty of the ionisation data, they seem to follow satisfactorily the same law of vapour-pressure.

It appears from the form of the proposed law that the hydration factor a makes very little difference to the vapour-pressure in weak solutions, which follow Raoult's law as a limiting case, but it makes a very great difference in strong solutions, when nearly all the free water is used up, and the denominator $N - an$ is small. Thus the depression of the freezing-point of a strong solution of calcium chloride is more than five times as great as that calculated from the number of ions present in the solution. Each ion appears to appropriate no less than 9 molecules of water. The factor $a = 9$ gives a very good approximation to the freezing-point curve, as far as the uncertainty of the data permit. When $N = an$, the vapour-pressure would be reduced to zero, according to the formula, but the formula ceases to apply when the vapour-pressure of the compound molecules themselves becomes equal to that of the solution. At or before this point the molecules will dissociate with the formation of lower hydrates. Many analogous phenomena are already known, and a

more complete study of the vapour-pressures of strong solutions may be expected to throw additional light on the subject.

The essential point of the theory here sketched is that the equilibrium existing in a solution is one between definite chemical compounds and the solvent, giving rise to a simple vapour-pressure relation by means of which the phenomena may be studied and elucidated. There is a great deal of work to be done before such a theory can be regarded as established, but in the mean time it may serve very well as a working hypothesis for correlating experimental results. and suggesting new lines of investigation. Regarded in this light, the vapour-pressure theory may serve a useful purpose, and judging by the experimental data at present available, I think I may fairly claim to have made out a good *primâ-facie* case for the theory.

[H. L. C.]

NOTE.—The vapour-current-indicator is a development of the old smoke-jack. A light spiral vane with a mirror attached is suspended in a tube which nearly fits it by means of a quartz fibre. Joule (Proc. Phil. Soc., Manchester, vii. 35) employed a wire spiral suspended by a silk fibre for indicating air currents, but does not seem to have adapted it for purposes of exact measurement. The instrument shown in the lecture gave a deflection of 30° (500 mm. at 1 metre) for a velocity of air current ·01 cm./sec. The sensitiveness might easily have been increased, but the above amply suffices for most purposes.

Friday, March 19, 1909.

GEORGE MATTHEY, ESQ., F.R.S. F.C.S., Manager,
in the Chair.

RICHARD THRELFALL, ESQ., M.A. F.R.S. Assoc.Inst.C.E. F.C.S.

Experiments at High Temperatures and Pressures.

WITHIN a few miles of this lecture room there is an unexplored region—to approach it we should have to move vertically downwards. It has been suggested by Mr. Parsons * that it would be worth while to make a short expedition in this direction, but the journey would be slow and the cost high- for instance, to bore a hole 12 miles deep was estimated to be a labour which would occupy eighty-five years and cost 5,000,000*l.* A well-to-do man desiring to benefit his fellow creatures could not do better than undertake this project, but till he comes forward we must perforce be content to try to imitate in our laboratories the temperature and pressure conditions which would be met with deep down in the earth.

Information, attainable from experiments under these conditions, is essential to the development of any exact concept of the structure and evolution of the earth. One of the most important questions in connection with the study of bodies under high pressures and at various temperatures is, as to whether any particular body is solid or liquid under specified conditions, and, if solid,-whether it is amorphous, glassy or crystalline. That pressure would influence the melting point of solids was clearly put forward by Clapeyron in 1834, but it was not till after the establishment of the mechanical theory of heat in the " forties " of the last century that the exact numerical relations could be established, as was done by Prof. James Thomson in 1851, when he calculated for the first time the amount by which the temperature of fusion of ice would be reduced by a given increase of pressure. The ideas underlying such calculations are based on a consideration of the way in which heat is converted into mechanical work in any prime mover depending on a heat-supply, and were first formulated by Carnot in 1824, before the true nature of heat was understood. As the matter is fully dealt with in every text-book, I will merely remind you that Prof. James Thomson was able to obtain an equation between the mechanical work actually produced under stated conditions and the work which, according to Carnot's principle, must be developed by a reversible engine operating between fixed temperature limits upon a given amount of heat.

* B. A. Reports, Cambridge, 1904, 672.

The general relation for a substance undergoing a change of state at absolute temperature T, such change involving a change of volume Δv and an absorption or emission of heat at constant pressure Q p, is, reserving the question of sign—

$$\frac{d\,T}{d\,p} = \frac{\Delta\,v\,T}{Q_p}$$

or in words, the change of melting-point produced by unit change of pressure equals the product of the absolute temperature, and the ratio of the change of volume of unit mass on melting to the quantity of heat absorbed or emitted by unit mass in the process.

Now the greater number of substances when they pass from the liquid to the solid state evolve heat and contract in volume. An increase of volume is of course a positive quantity, and if heat is absorbed during this increase it is reckoned positive also. In the case of water, heat is evolved during freezing as in other cases, but the mixture of ice and water has a smaller volume than the solid ice. Accordingly the change of volume in this case is negative, and the melting-point falls as the pressure rises.

The first fairly exact confirmation of the theory appears to be due to De Visser,[*] who selected acetic acid most carefully purified as a test substance— though valuable experiments up to much higher pressures had been previously made by many others—particularly by Dewar on water,[†] Ferche on benzol,[‡] and Damien[§] on a variety of substances.

It is necessary to work with a pure substance in order to test the theory, or at all events with one whose solid phase has the same constitution as its liquid phase. If the acetic acid had not been pure the probability is that the frozen part would have contained more or less of the impurity than the unfrozen, and consequently a state of affairs not contemplated in the theory would have arisen. From the experimental point of view it is obvious that a sharp melting point is a necessary condition for its accurate observation.

A quantity of acetic acid—rather over 40 c.c.—is confined by mercury in a closed apparatus based on a previous design by Bunsen, which also contains air in a graduated tube. When the acetic acid melts it expands and compresses the air through the intermediary of the mercury—whereby the pressure can be inferred. The part of the apparatus containing the acetic acid is immersed in a bath which can be kept at any desired temperature. As the melting progresses a pressure is set up by the expansion, and finally attains such a value that no further melting can take place. We then have a mixture

* Recueil des Travaux Chimiques des Pays-Bas, xiii. 1893, 101.
† Proc. R. S., xxx. 1880, 533.   ‡ Wied. Ann., xliv. 1891, 265.
§ C. R., cxii. 1891, 785.

of solid and liquid acetic acid in presence of each other under a measured pressure and at a known temperature. The quantities entering into the calculation are ascertained from other experiments— notably the ratio of the change of volume to heat absorbed was ingeniously ascertained by a modification of Bunsen's ice calorimeter. The final result was that the rate of variation of temperature of melting-point with increasing pressure was calculated to be $0 \cdot 02421°$ C. per atmosphere as against $0 \cdot 02435°$ C. found by experiment—a differ- ence of $0 \cdot 57$ per cent. I have dwelt on this work at some length in the hope that it may make the nature of the problem clear. It is to be noted that the experimental difficulties are considerable, and are enhanced by the fact that we have no à priori reason to suppose that the rate of change of melting-point with pressure is a constant quantity independent of the pressure. In fact it was shown by Sir Joseph Thomson about 1886 * that in calculating the change of melting-point we ought to take into consideration "the difference between the energy due to strains produced by the pressure in unit mass before and after solidification." Sir Joseph Thomson's reason- ing, based as it is on a generalised Lagrangian method of treating problems involving energy changes, is unsuited for discussion in a non-mathematical address, but it is easy to see that if the compressi- bilities of liquid and solid are different, then the change of volume accompanying the change of state of unit mass must itself depend on the pressure, and therefore the pressure change of melting-point which is proportional to the change of volume must depend on the square of the actual pressure so far as this part of the effect is concerned. This anticipation was realised by Damien in 1891, who showed that the melting-points of substances in terms of the pressure could be expressed by a formula of the kind

$$t = t_0 + a\,(p - 1) - b\,(p - 1)^2$$

t_0 being m.p. under 1 atmosphere pressure.

I think we may add that there will also be a small effect depend- ing on changes of energy in the capillary layer separating the phases.

The first adequate investigation of the change of m.p. under pressure over a wide range of pressures was made by Barus.† Time does not permit me to do more than exhibit the results obtained, though the apparatus employed was most cleverly designed. It requires great experimental knowledge and ingenuity to infer with accuracy changes of volume of a few per cent. of the original volume at pressures of 1500 atmospheres, nearly 10 tons per square inch. If we note the pressures and temperatures of melting, and plot the result as a curve against the pressure and temperature, we obtain what is

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* Applications of Dynamics to Physics and Chemistry, 259.
† Bulletin No. 96 of the U.S.A. Geological Survey, 1892.

called a melting-point curve, and this divides the field into two parts, so that on one side of the curve the temperature and pressure at each point have such values that the substance is solid, while on the other side their values are such that the substance is liquid. It is instructive, therefore, to regard the melting-point curve as the line separating the region of solid from the region of liquid. Along the line, and along it only, i.e. at the pressures and temperatures indicated by points on the line, the solid and liquid phases can exist in equilibrium together. Such a diagram is called a " Diagram of Condition."
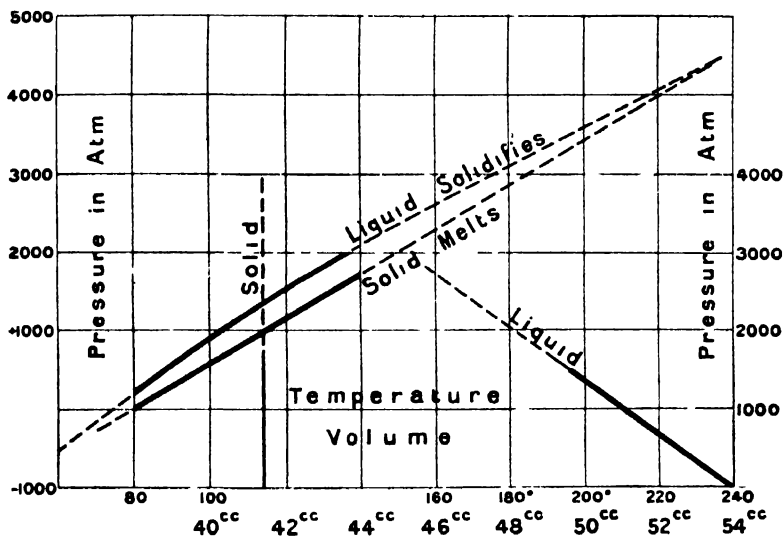
FIG. 1.

Full lines indicate party field actually explored.
Dotted lines indicate extrapolations.

By far the greater part of our information as to the quantitative relations of bodies at high pressures we owe to Prof. Gustave Tammann, who has collected his results in a book entitled " Kristallisieren und Schmelzen," whose advent (1903) must be regarded as an important event in the history of the subject.

The complete thermodynamic specification of a body involves a knowledge of its mass, volume, pressure, temperature, energy, entropy, surface tension, and nature—whether liquid, solid, glassy, crystalline or amorphous.

Prof. Tammann has simultaneously measured the pressure, temperature, volume and mass of many substances under high pressure, and at temperatures extending from 80° to 200° C.—taking cognizance

of the physical state—and has thus been able to plot out many interesting diagrams of condition. The apparatus consists of a screw press by which a piston of ebonite is driven down a steel cylinder of small known cross-section. The cylinder is filled with oil, and the ebonite piston fits practically oil-tight. The oil communicates with the oil contained in a strong steel vessel, which also incloses a glass tube open at the lower end, containing the substance and dipping below the level of mercury contained in a dish. The oil occupies the rest of the space. The steel vessel is placed in a thermostat so that its temperature can be ascertained. The oil pressure is measured by a Bourdon gauge which it was possible to standardise, thanks to the previous work of Amagat and Tait. In order to construct a diagram of condition it is necessary and sufficient to find a number of points separating the liquid from the solid area—or separating the areas corresponding to different crystalline forms in the case where the transformation of one sort of crystal into another is under investigation. To understand how this is done, it is best to take a special case. If we have a quantity of a substance under a known pressure and temperature in the piezometer and suddenly increase the pressure, so that there is not time for heat to pass in or out to any appreciable extent before the pressure gauge can be read, we have practically adiabatic compression. If the apparatus be then left to itself, the heat which we may suppose to be liberated by the pressure will slowly diffuse outwards, and the pressure will fall as time goes on. If we happen to start from a point on the m.p. curve before the pressure is raised—then the final result will be that we shall thaw or freeze more or less of the material, and the original pressure will be exactly regained, the change of state compensating the impressed change of volume. If, however, the increase of pressure has been so great that a change of state of the whole mass has been brought about, then the after variation of pressure will be so much greater that it is easy to distinguish this case from the previous one.

The accompanying diagram (p. 546), taken from Prof. Tammann's book, shows how the equilibrium curve can be located in the case of carbon dioxide and naphthalene. In the former case the temperature was $0.31°$ C. The pressure was 3800 kilograms per sq. cm., or 24.13 tons per sq. inch. (157.49 kilograms per sq. cm. = 1 ton per sq. inch = 152.38 atmospheres.)

The pressure was raised adiabatically to 4400 kg./cm.² (27.93 tons/sq. inch) and the subsequent fall of pressure plotted against a time scale for ten minutes. The pressure was then adiabatically reduced to 3550 kg./cm.² and the recovery curve again plotted. The equilibrium pressure must lie between the pressures approached asymptotically on the diagram, i.e. between 3825 and 3792 kg./cm.². A repetition between narrower pressure limits enables the pressure to be fixed at between 3808 and 3798 kg./cm.². A similar procedure fixed the pressure of the m.p. of naphthalene between 3090 and 3080
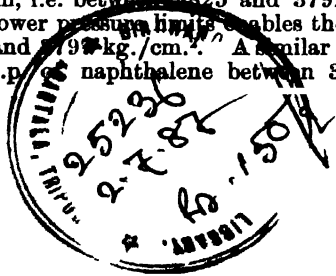
kg./cm. at the temperature considered—a difference which corresponds to $0\cdot2°$ C., the actual temperature possibly differing from the thermostat temperature by $0\cdot1°$ C.

We may now pass on to the consideration of some of the results obtained, which refer not only to change of melting-points, but to changes in the temperatures of transformation of isomorphic forms.
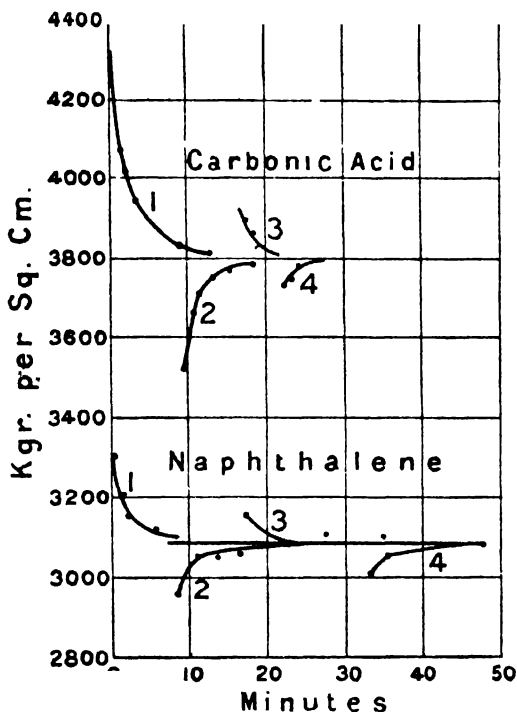
FIG. 2.

As illustrations of such changes, I show here the transformation of yellow to red mercuric iodide, which shows well in the projection microscope ; also Mitscherlich's transformation of potassium bichromate, and sulphur in two forms.*

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* *Experimental Demonstration of a Transformation of Sulphur.*—A microscope slide is prepared by partially melting a fragment of monoclinic sulphur, and inclosing some of the melt between the slide and cover-slip, well pressed together. The presence of unmelted monoclinic sulphur insures the crystallisation of this variety on lowering the temperature. By means of a hot stage it is possible to preserve the crystallisation long enough to exhibit it by means of a projection polarising microscope. The appearance is very charac-

The case of sulphur is one of great interest. It has long been known that sulphur can exist in at least three solid forms. It crystallises from some solvents in octahedral crystals, from others or from its liquid state in monoclinic crystals. In the latter case some amorphous sulphur is generally dissolved in the crystals, and the amorphous variety itself is formed in tough vitreous masses when molten sulphur heated till it becomes very viscous is poured into cold water. At ordinary temperatures the octahedral form alone is stable. It has been found that at atmospheric pressure octahedral sulphur is converted into monoclinic at $95 \cdot 4°$ C. and in the process $2 \cdot 7$ gramme-calories per gramme of sulphur are evolved. The density of octahedral sulphur is about $2 \cdot 03$ and of monoclinic about $1 \cdot 98$ at ordinary temperatures. In accordance with the principles developed previously the transformation temperature of rhombic to monoclinic sulphur must rise with increase of pressure. So far back as 1887 Roozeboom[*] was able to predict that the diagram of condition for sulphur would be as shown on the next page.

Prof. Tammann has supplied the corroboration of the existence of the triple point.

Suppose that we have sulphur at a pressure of about 1500 kg./sq. cm. ($9 \cdot 52$ tons/sq. inch) and raise its temperature to about 160° C. or more, we shall cut the melting-point curve of octahedral sulphur, and the sulphur will melt. If we then allow the sulphur to cool, keeping the pressure up, octahedral sulphur will crystallise from the melt instead of monoclinic sulphur. This very likely has some bearing on the occurrence of native crystals of octahedral sulphur.

It is not every substance which has such sharply defined properties as sulphur, though even these are not as sharp as they might be, owing to the constant presence of amorphous sulphur. An instructive case is afforded by phenol. As the diagram shows, there is a considerable region of the field in which two kinds of crystals of different density can exist together, the curves forming the boundary of this region of pseudo-equilibrium.

It may be that the two crystalline forms of carbon which ap-

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teristic. Another slide is prepared, but this time all the sulphur is melted, and can generally be undercooled so far that it crystallises in what is believed to be the octahedral system. This slide is then placed in the projection microscope, when it is seen that its appearance is totally different from that of the first slide. The preparation is then heated on the hot stage, and when the transformation temperature is reached it is seen that the structure begins to change—the crystallisation breaks up and becomes granular, the granules showing in general much more colour than the original crystallisation. These granules are taken to be monoclinic sulphur. The temperature is now raised till about half the preparation has melted, and it is then allowed to cool back a little so as to crystallise. The crystals now show the characteristic mono clinic crystallisation with brilliant colours, since unmelted monoclinic sulphur is present.

[*] Rec. Trav. Chim. Pays-Bas, vi. 1887, 314.

parently can exist together indefinitely at ordinary temperatures and pressures are an illustration of the same property.

As a final illustration we may note the results for water down to − 80° C., from which it appears that it possesses three allotropic crystalline forms with at least two melting-points.
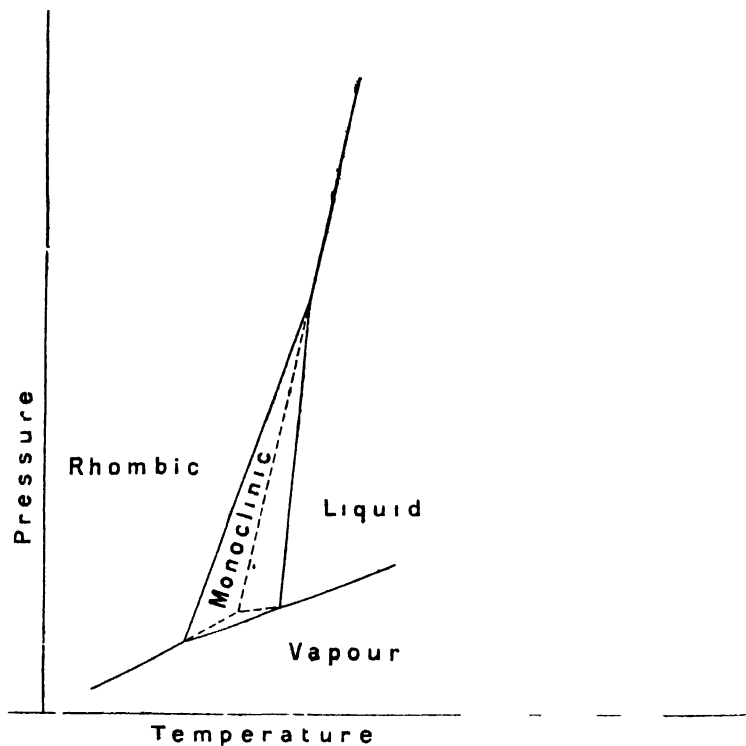
Fig. 3

The melting-curves of from thirty to forty substances have been investigated, mainly by Tammann, up to about 3000 kg/sq.cm. = 19·05 tons/sq. inch, and the general result has been to show that there is a tendency for the rate of change of melting temperature with pressure to fall off as the temperature rises, and also that many substances, which at ordinary pressures crystallise in one form only, can be caused to assume allotropic modifications under high pressure. This tendency to form allotropic modifications appears to be associated with the extent to which a substance can be under-cooled without crystallising.
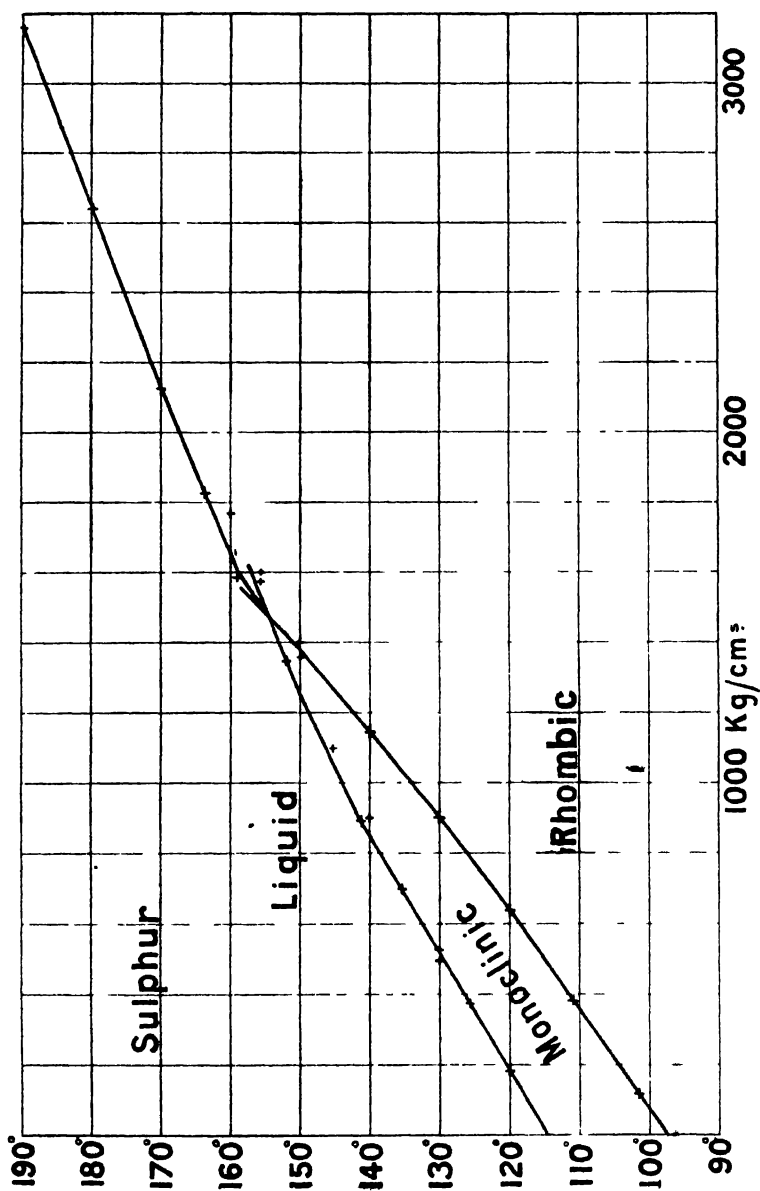
Fig. 4.

A question of the greatest interest and importance may now be formulated—what will happen if we go on increasing the pressure?
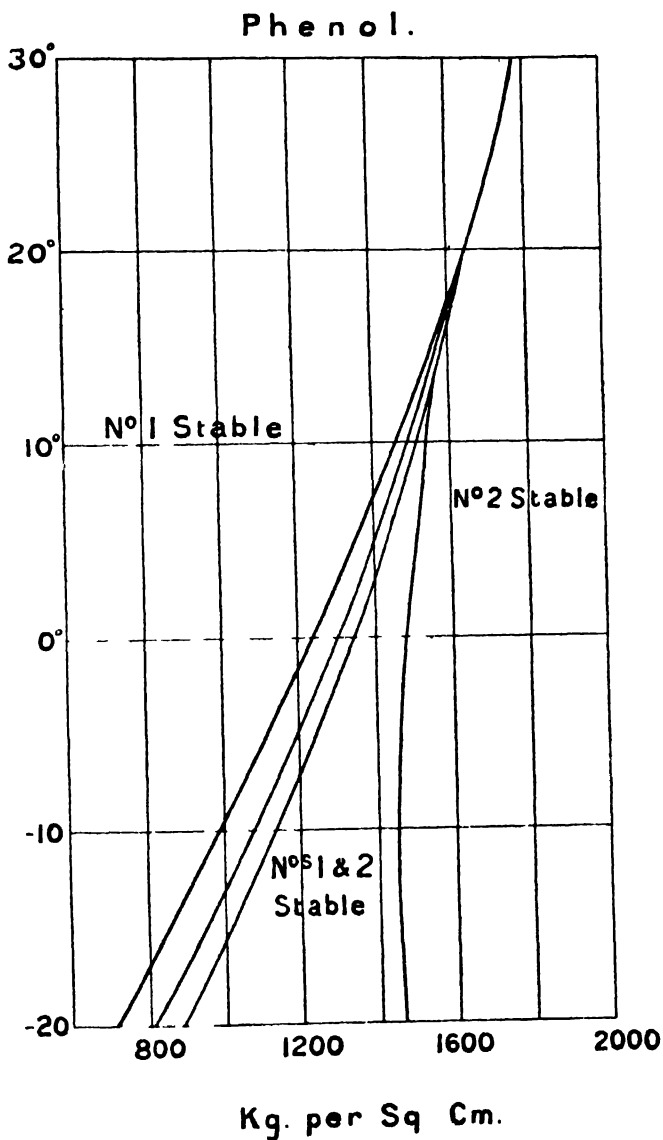
FIG. 5.

Will a state of affairs be reached in which it is no longer possible to distinguish between the liquid and its crystalline form ?   Will there be, in fact, a sort of critical point at which the melting-curve will end ? At present we can only say that no indications of such an occurrence have been observed experimentally, and Prof. Tammann takes the point that it is highly improbable that anything in the nature of continuous transformation can take place, because a crystal has different properties in different directions related to its axes, and there is thus a much greater qualitative difference between crystals and liquids than between liquids and gases, both of which are isotropic.   I must admit that this argument does not appeal to me very strongly.   If it be possible to compress a substance till it reaches a state in which, at one and the same temperature, the liquid has the same density as the crystals, presumably the mean distance of the molecules will be the same in both cases.   I see nothing monstrous in the view that under these circumstances crystallisation may set in gradually, and that it may not be possible to say exactly when the liquid ceases to be a fluid and becomes a crystalline solid.   There are no theoretical or other grounds for supposing that the phenomena of crystal growth as observed when there is a change of volume accompanying the crystal formation, will necessarily hold when no such change of volume occurs.

If we refer to the theory of the change of m.p. by pressure it is obvious that if either the change of volume or the latent heat of melting vanish at any temperature or pressure on the melting-curve, then in the neighbourhood of this pressure the curve must degenerate to a point—or small pressure changes will not affect the m.p.   It was pointed out, however, that there is a term or terms depending on the square of the pressure, and if these were relatively important the only thing we should notice would be a change of curvature at the point under consideration.   It does not follow that there is no maximum or minimum to the melting temperature of any particular substance because the term in P^2 may be vanishingly small : it may be (and generally is) of opposite sign to the term in P, and in this case it is only a question of the relative importance of the terms where the maximum or minimum melting-point lies. Damien's empirical formula expresses precisely the effect to which I refer.   The practical result which is of importance in questions affecting the condition of the inner layers of the earth is that we are not entitled—in fact, it is wrong—to suppose that pressure must necessarily go on raising the melting-point indefinitely ; everything depends on the substance under consideration.   It is therefore necessary to make such experiments as those of Tammann at vastly higher temperatures and pressures than those we have been considering, up to probably over 10,000 kilograms per sq. cm. (or $63\cdot6$ tons per sq. inch).

In 1893 some experiments were described by Parsons * in which

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carbon rods were heated by electricity under a pressure usually of 15 tons per sq. inch—but rising in one case to 30 tons per sq. inch. The pressure was obtained by means of a hydraulic press, but no detail is given.

I have been desirous for many years of making some experiments at high temperatures and pressures, but for a long time could think of no way of ascertaining the pressure at temperatures over a red heat except by the use of compressed gases. In 1902 Sir Andrew Noble was kind enough to have some drawings prepared for a wire-wound steel pressure vessel to carry a pressure of 50 tons per sq. inch. The pressure was to be supplied by a compressed gas, and some details of the heating arrangements were designed, when a calculation of the cost of the gas compressors, vessel and appurtenances made it clear that the undertaking would be beyond my means. I then endeavoured to find a simpler form of apparatus, and finally was led to contemplate the substitution of graphite for compressed gas, Spring having pointed out that crystalline graphite flows very easily at high pressures. A simple trial made it clear that the graphite of Ceylon does in fact possess the property of flowing like a liquid under high pressure to a sufficient degree to allow of pressure being transmitted by it. Graphite can be used with some reservations to transmit a pressure just like water or oil, though it is, of course, inferior in fluidity, and as I have now discovered occasions a loss of "head" which is not independent of the pressure itself. My former statement in the 'Chemical Society's Journal,' 1908, is erroneous, though the results of the experiments are, I believe, hardly or not at all affected by the mistake for a reason which will be clear later on. After several trials, the apparatus which I have here to-night was evolved, and some experiments were made with it. These experiments are not of any great importance, and, indeed, I feel almost ashamed of bringing them to your notice—I can only say in excuse that everything must have a beginning.

I believe, however, that the apparatus is sufficiently simple, cheap, and effective, to enable others with more leisure at their disposal to make a beginning of an investigation of the properties of matter up to 100 tons per sq. inch, and at temperatures up to about 2000° C. At present, however, it is not possible to infer with accuracy the volume of the substance under these extreme conditions, nor can its physical condition be more than approximately and indirectly inferred —we must content ourselves with the production of transformations which we can make persist down to ordinary temperatures and pressures.

If we refer again to the sulphur diagram, we shall see how this possibility may arise. If sulphur is melted and cooled slowly mono-clinic crystals are found—when the temperature sinks below 98° C. these crystals undergo spontaneous transformation to the rhombic form—but all that we see is that the monoclinic crystals become

opaque : the external form of the crystals is still monoclinic, but they are merely pseudomorphs of the original crystals. To obtain large octahedral crystals we may suppose that we begin by melting sulphur and raising the temperature and pressure till the former stands at 160° C. or over, and the latter at not less than 1600 kg./cm.^{2} (10·16 tons/sq. inch).

If we then slightly reduce the temperature or raise the pressure, we shall have the crystallisation of the sulphur in the rhombic form. By maintaining the pressure as the mass cools and when it is cold releasing the pressure, we should finally extract rhombic crystals. To this we may of course add that we need not expect crystals of any size unless we cool at the proper rate. It appears that there are at least two phenomena requiring attention in relation to the production of crystals—one is the relation between the amount of undercooling necessary to induce spontaneous crystallisation, and the other is the rate at which the crystals will grow when they have once started. If we want large crystals, we must not have an excessive number of points of spontaneous crystallisation ; nor must we have too high a rate of crystal growth, or the crystals will by all experience tend to be felted together. The temperature condition giving birth to the most favourable number of spontaneous centres is not necessarily the temperature at which crystals grow to the largest size, so there is really no escape from finding by direct trial the most effective way to go to work.

Another possibility is brought to light by an examination of a case of pseudo-equilibrium such as that of phenol. Here we have three regions—in one No. 1 alone is stable, in another No. 2, and in the third both Nos. 1 and 2 are stable. The case of iodide of silver is similar, but more complicated. If in the area C we change the pressure, the temperature remaining constant and the material consisting of a mixture of the two stable phases, we can alter the proportions in which these phases exist, but we cannot cause either of them to disappear.

A notable case of this kind is that of graphite and diamond, both perfectly stable in presence of each other at atmospheric pressure up to a temperature nearly that of the electric arc, say about 3000° C. If there be any similarity between the carbon and phenol diagrams, diamond would correspond to variety No. 2 of phenol, and graphite to variety No. 1, heat being evolved in both cases when the less dense modification changes into the denser. If we desire to obtain phenol 2 from phenol 1, we note that down to a temperature of − 20° C., we should require to keep the pressure always above about 600 kg./cm.^{2} ; otherwise the operations would be similar to those described in the case of rhombic sulphur.

Similarly, to convert graphite to diamond on this analogy we should have to raise the temperature and pressure together to some unknown values and then let the product cool—keeping up the pressure meanwhile.

The apparatus which I have used in making the experiment is based on the transmission of pressure by crystalline graphite or the softer metals. In order to ascertain how much pressure is lost during transmission I have arranged an apparatus in which the material to be tested is exposed to a known pressure, tending to force it through a cylindrical space, identical in figure with the space in which the heating is intended to be carried out. The pressure transmitted is transferred by a simple device to a piston with a hard steel point, and this is forced by the pressure to penetrate a soft steel plate. In a subsequent experiment the same piston is forced by a known pressure into the same steel plate, so as to penetrate to the same depth as in the main experiment. It is then possible to compare the pressure transmitted with the pressure applied.

Experiments of this kind have been made with lead and with graphite as pressure transmitting substances.

So far as I know, there is no substance other than graphite combining the property of a certain amount of fluidity with the capacity to resist high temperatures ; and our hope of studying chemistry at really high pressures and temperatures appears at present to depend largely upon it. It is true that some attempts have been made to use compressed gases, but the apparatus is vastly more complicated, and the experiments themselves become really dangerous in view of the immense potential energy possessed by gases at pressures of 100 tons per square inch. As illustrating this I may mention that 100 tons per square inch is about the highest instantaneous pressure noted by Sir Andrew Noble in his well-known experiments on the exploding of cordite in closed vessels. The density of nitrogen at 100 tons per square inch is, taking Boyle's law as a very rough approximation, 15,240 times its density under standard conditions. This works out to rather over 19—i.e. about the same as gold, and the energy stored is of the same order as that contained in an equal volume of cordite, though its availability is lower.

The construction of the apparatus I have used can be easily followed from the drawings. It consists essentially of a steel cylinder divided perpendicular to the longitudinal axis by a thin plate of mica : the two halves being clamped tightly together by an insulated ring and clamps at top and bottom. Pressure can be applied by an ordinary hydraulic lifting jack—the one I have used will lift fifty or sixty tons—the bore of the hydraulic cylinder being about 4½ inches. In order to operate at a high temperature it is necessary to line the cylinder with some refractory substance, and I have generally used magnesia for this purpose, though zirconia or thoria might be better. Purified magnesia is first melted in an electric furnace and then ground in an iron mortar till it is very fine. The powder is freed from iron as well as possible by a strong magnet, and after being sifted is pressed into the cylinder little by little by hydraulic pressure so as to form a solid
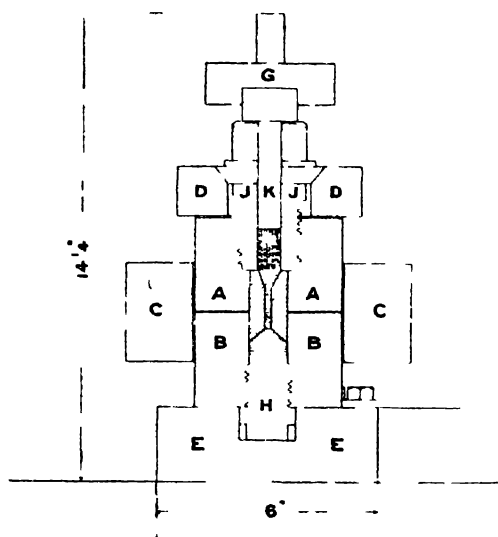
Fig. 6.
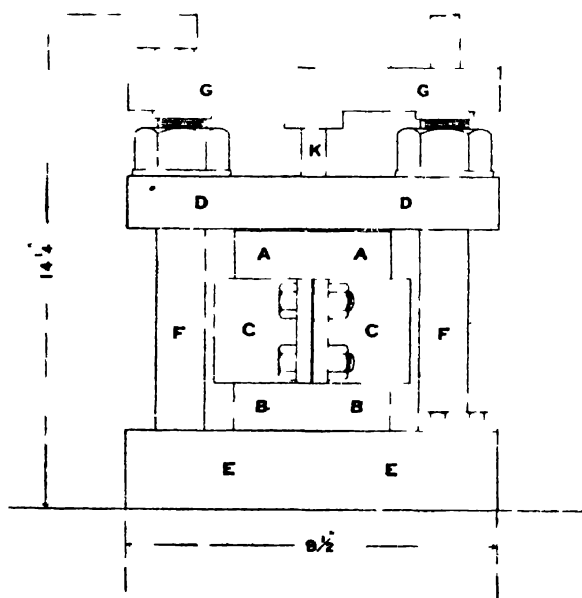
Fig. 7.

plug.   This is then bored out with a hard steel drill to the required diameter.   In pressing magnesia I have found that it is not possible to thoroughly consolidate the powder in greater thickness than a few millimetres, even under a pressure of 50 tons per square inch.   In fact magnesia is a substance which appears to be almost devoid of the fluid properties so marked in graphite—an essential condition for its use in the apparatus.   I have tried various other linings, ground flint, alumina, etc., but they have no advantage over magnesia, and are even more difficult to drill out.   Alumina prepared from the crystalline hydroxide is very easily compressed into cakes, and makes a good lining, but it is too fusible for experiments on carbon, and is
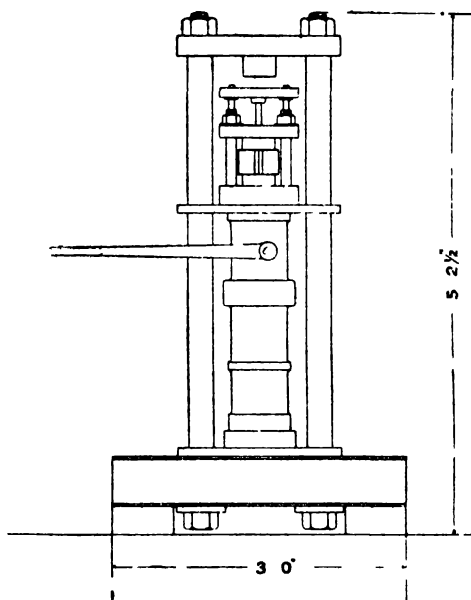
FIG. 8.

probably more easily reduced.   The cylinder having been lined, the bottom is filled in with Acheson graphite in electrical communication with the base of the apparatus.   The substance to be operated upon is placed in the narrow part of the bore, and packed in with graphite or lead if that is suitable.   The pressure is applied by a ram of hardened high speed steel, working upon a reservoir of graphite or lead contained in the plug closing the cylinder at the top and electrically connected to the other terminal of the supply.   The chief uncertainty in regard to the pressure which actually reaches the subject of the experiment lies in the possibility of the ram being

held to some extent by friction against the sides of the cylindrical hole in which it works, and in the consolidation of the graphite—with reduced fluidity, before it actually flows. One has to trust either to the hardness of the ram or to leave a space round it sufficient to allow graphite to escape, when the apparatus follows the lines of Amagat's standard pressure gauge, but the duration of the experiment is curtailed by the exhaustion of the graphite supply. A connection has to be applied for the pressure absorbed by the lead or graphite in accordance with the results of the preliminary trial. It is fair to say that no tendency of the ram to stick has ever been noticed -on the contrary, changes of volume brought about by heating have made themselves evident at once on the pressure-gauge of the hydraulic press.

When working with any form of carbon there has been no trouble in arranging to heat the body which is being compressed by electrical means. It has been found most convenient to adjust the current to about the value required by means of a resistance—large compared with that of the pressure vessel—the latter being short-circuited meanwhile. In making an experiment, the hydraulic press is worked till the desired pressure is attained, and then by opening the switch the current is thrown on to the apparatus. When the magnesia lining begins to melt, the pressure, as shown by the pump gauge, is seen to fall, graphite flows into the magnesia tube, and the pump is worked so as to compensate for this. Under these conditions the pressure is probably transmitted without appreciable loss, as the narrow part of the cylinder is now in a fluid bath. After a sufficient time has been allowed the switch is closed and the pressure kept up by pumping till the apparatus is cold. Originally an apparatus with a cylinder made in one piece was employed, and in this case there was a considerable voltage between the graphite entering the apparatus and the steel walls of the pressure vessel. After a few seconds of intense heating it frequently happened that an explosion took place, due (as could be seen by subsequent examination) to filaments of graphite being driven through the magnesia and producing short circuits against the steel vessel. With the construction above described these explosions do not occur, and there is the additional and very real advantage that when an experiment is over the apparatus can be opened in the middle and everything exposed to view.

A large number of experiments were made on different kinds of carbon and graphite. The weight of material in the highly heated part was generally from 1 to 2 grammes, and the energy supply was at a rate of 5 to 10 kilowatts for from three to six seconds. The pressure in a successful experiment lay at from 50 to 100 tons per square inch throughout. The magnesia lining was usually melted for a distance up to 1 centimetre round the graphite. Now magnesia melts at ordinary pressures at about 2000° C., but the energy supply

is sufficient to render it possible that temperatures of from 3000° to 4000° C. may have been reached ; it is possible that about 3000° C. was actually attained at the centre of the charge. The results obtained were uniform. No matter what form of carbon (excluding diamond, which was not tried) was packed originally in the apparatus the final product was soft well-crystallised graphite ; which agrees with some results of similar experiments described by Mr. Parsons,* but not with the results claimed by Dr. Ludwig.†

In several experiments the crystalline mass of graphite was tested in regard to its porosity, and this was found to be considerable - a remarkable result, having in view the conditions under which it had been formed.

Another point of interest was that where the soft graphite had been driven into the Acheson graphite plug at the bottom of the apparatus it became extremely hard, so much so that a hard steel file made little or no impression upon it.

The main difference in treatment of this part of the graphite as compared with the remainder is that it was cooled much more quickly, thanks to the high heat conductivity of the Acheson graphite plug. The cause of hardening has hitherto not met with any satisfactory explanation.

No appreciable quantity of carbide of magnesia was formed in the experiments. The magnesia close to the graphite core contained traces of carbides, but as there were always traces of iron left from the drilling out process, this may be plausibly accounted for by the formation of carbide of iron.

The graphite was finally systematically searched for microscopic diamonds by Staudenmaier's modification of Brodie's method of conversion of graphite into graphitic acid,‡ or else by Moissan's modification of the same method.§ A convenient means of distinguishing diamond in fine powder from most or all of the substances which are not separated by a liquid of density 3·34 at 4°C. is to heat the powder in a silver spoon to a dull red heat in fused potassium hydroxide. Check experiments showed that diamond dust easily passing a sieve with 100 threads to the inch would withstand the action of molten caustic potash at a temperature at which the edges of the silver spoon began to melt, for five or ten minutes. Crystals of alumina or of carborundum are entirely destroyed by this fusion, but the diamond particles seemed to have undergone no change. In fact the individual fragments could be recognised under the microscope after passing through the ordeal.

I am led to consider that my experiments indicate that no wholesale transformation of amorphous carbon or graphite into diamond

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* Proc. R.S., 79.   † Zeits. für Electrochemie, 1902, 273.
‡ Ber. 1898, xxxi. 1485.   § Electric Furnace, 49, translation.

can be brought about by temperatures of the order of 2000°C., and pressures of more than 50 and less than 100 tons per square inch. There is some uncertainty, as already mentioned, in regard to the actual pressures operative during the trials. Prof. Tammann has, however, obligingly drawn my attention to the fact that the equilibrium curve graphite-diamond may nevertheless have been crossed, but that no diamond was formed because time for crystallisation was not allowed under the conditions of the experiment. I confess my idea in making the trials was that the amorphous carbon or graphite might be forced to melt, and then that the conditions would require it to recrystallise as diamond—not, of course, in the form of large clear crystals, but rather in the style of bort or black diamond. It is, however, true that the pressures used may have prevented any melting at all, and that it may have been a question of recrystallisation of graphite, in which case the addition *ab initio* of diamond crystals would, as suggested by Prof. Tammann, have been of advantage in promoting crystallisation in that form.

The experiments described have only been rendered possible by the invention of high speed steel, which keeps its hardness up to nearly or quite a red heat, and any further advance mainly in the direction of the allowance of more time —must wait for improvements in that n 'erial. It may very well be, however, that the limits of temperature within which crystallisation in diamond form can take place, are really very narrow at any pressure—and in this case it will be a matter of very great difficulty to make an apparatus in which the conditions could be kept constant for a sufficient length of time—and the difficulty would be greater the higher the temperature.

It is noteworthy from this point of view that in Moissan's artificial production of diamond very much lower pressures and temperatures were used than those just described. I have shown* that, using iron as a solvent, it is highly improbable that Moissan attained a pressure of more than 20 tons/sq. inch, and when silver was employed the pressure would be much lower. A similar criticism places the effective temperature of formation of diamond in iron or silver spheroids at something of the order of 1500° C. Comparing the experiments of Moissan with those described above, it looks as if Roozeboom's opinion is at present the most probable—viz. that solvents are necessary in order to depress the crystallisation point of diamond to a temperature at which the transformation to graphite is slow enough for rapid cooling to interrupt it. In this case the next step would be to repeat the experiments I have described at the highest possible pressure in the presence of iron, though Mr. Parsons† has already made some trials in this direction with negative results. We have, however, many

* Journ. Chem. Soc., xciii. 1908, 1351.   † Loc. oit.

metals which have never been tried in this connection, and one or other of them may turn out to have the requisite properties.

I desire to acknowledge the assistance I have received in making the experiments described from my assistant Mr. C. H. Beasley, and in examining the products from Mr. T. H. Waller.

[R. T.]

Friday, April 2, 1909.

SIR WILLIAM CROOKES, LL.D. D.Sc. F.R.S., Honorary
Secretary and Vice-President, in the Chair.

PROFESSOR SIR J. J. THOMSON, M.A. LL.D. D.Sc. F.R.S. *M.R.I.* ;
Professor of Natural Philosophy, Royal Institution.

Electrical Striations.

ONE of the most conspicuous features of the electric discharge through
gases, when the pressure is within certain limits, is the exceedingly
well-marked alternations of light and darkness which occur in the
positive column.   These alternations, which are called striations, are
so varied and beautiful that since their discovery by Abria in 1843
they have attracted the attention of many physicists.   Grove, Gassiott,
Spottiswoode and Moulton, De la Rue and Müller, Crookes, Wood,
Skinner, H. A. Wilson, and Willows, have published important re-
searches on the conditions under which the striations are produced ;
on the influence upon them of such things as the nature and pressure
of the gas, the size of the tube, the current passing through it ; and
on the distribution of the electric force in the neighbourhood of a
striation.   The investigations described in the following paper relate
for the most part to the last of these questions, and were made with the
object of testing a theory of the striations which I gave in my Treat-
ise on the Conduction of Electricity through Gases.   For these experi-
ments I used tubes fitted with Wehnelt cathodes, i.e. the cathode was
a strip of platinum-foil heated to redness, and having on it a spot of
lime or barium oxide.*

With these cathodes large currents can be sent through the tube,
and remarkably bright and steady striations obtained at lower pres-
sures and with smaller potential-differences than with the ordinary
type of discharge.   The pressure has, however, to be low, consider-
ably less than 1 mm. of mercury, to get the full advantages from
these cathodes.   The first point to which attention was directed was
the distribution of electric force along the line of the discharge.   In-
vestigations on this point have already been made by Skinner and
H. A. Wilson, but it seemed to me that the steadiness of the striations

* My assistant, Mr. Everett, has found that these cathodes can be very
easily made by letting a drop of sealing-wax fall on the foil, and then burning
away the combustible matter by heating the foil to incandescence.   Sealing-
wax seems to contain large quantities of some salt of barium.

with the Wehnelt cathode made this method of investigation particularly suited for these investigations. The first method used to measure the variations in the electric force along the discharge was to find the variation in the difference of potential between two platinum wires 1 mm. apart as the wires were moved from the cathode to the anode. Several devices were used for this purpose : in some the platinum wires (surrounded up to about a millimetre from their tips with glass rods) were carried on a sort of railroad and moved from cathode to anode. The electrodes in the discharge-tube in this case were fixed. The measurements of the potential-differences made by this method at low pressures gave the very remarkable result that just on the cathode side of the bright part of a striation the electric force was negative (i.e. that the force on a positive charge was in the direction from *cathode to anode*) : on crossing over the bright boundary to the anode side the electric force at once became positive, and rose to

Fig. 1

Fig. 2
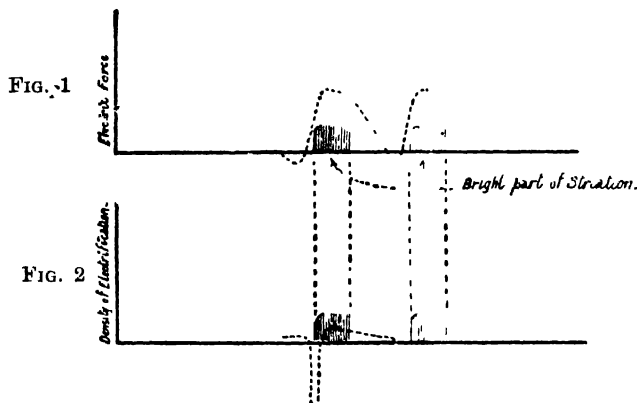
a high value. It soon, however, began to diminish, and went on diminishing up to the cathode side of the bright part of the next striation on the anode side. The distribution of the electric force in the striation is represented in Fig. 1, and the corresponding distribution of positive and negative electricity in Fig. 2, the ordinates representing the distribution of the electrification both as to magnitude and sign. Thus if these measurements of the electric field can be relied on we have intense negative electrification at the bright head of a striation (by head is meant the side next the cathode), and a weak positive electrification through the rest of the field. The transition from positive to negative force was very abrupt and well marked, so much so indeed that the position of the platinum wires in the striation could be ascertained with great accuracy without looking at the discharge, by observing the deflexions of the electrometer by which the potential-difference between the wires was measured.

Many changes were made in the way in which the wires used as detectors were arranged; thus, to prevent any screening of the one wire by the other, an apparatus was used in which the two platinum wires were brought in from opposite sides of the tube, so that there should be no overlapping; exactly the same results were obtained with this apparatus as with the other.

Again, another arrangement, similar to one previously used by Professor H. A. Wilson, was tried, in which the exploring electrodes were kept fixed, and the anode and cathode kept at fixed distance apart were, by means of a float, moved relatively to the exploring electrodes *a b*, so that these could occupy all positions from the anode to the cathode. The arrangement is represented in Fig. 3. The exploring electrodes in some of the experiments protruded about a millimetre beyond the ends of the glass tubes into which they were sealed: in other experiments very fine hollow glass tubes were used to cover the wires, and the wires instead of protruding beyond the glass stopped short at about a millimetre from the end of the tube; this arrangement was adopted with the idea of protecting the wires against streams of corpuscles coming down the tube: these by giving up their charges to the wire might cause this to acquire potentials different from those of the gas at the tips of the wire. The results obtained with all these modifications were exactly the same as those obtained with the first type of apparatus, i.e. there was always when the pressure of the gas was low a negative electric force just
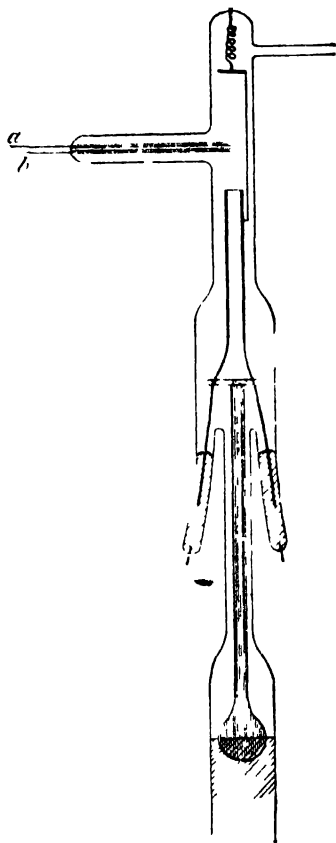
Fig 3.

in front, i.e. on the cathode side of the bright part of a striation; this changed to a large positive force as soon as the bright boundary of the striation was passed; at a short distance from the front of the striation this force began to diminish and went on diminishing until the front of the next striation on the anode side was reached.

Though the indications of all these wire explorers agreed in pointing to the existence of a negative force in front of these striations,

yet I felt that the existence of a negative force could never be proved by the use of wire detectors.

For let us consider what the existence of a negative force implies. The electric current is always in the same direction throughout the tube, and therefore the average movement of the ions is in the same direction at all parts of the tube ; thus, whenever the electric force is negative, there must be ions moving against the electric force instead of with it. Now the validity of the method of the wire electrodes depends upon the assumption that the ions in the neighbourhood of the tip of these electrodes follow the lines of force, that if, for example, the tip were at a higher potential than the gas so that the force on a positive ion were away from the tip, negative ions would follow the direction of the force acting upon them, and run into the tip and lower its potential until it became the same as that of the gas in its neighbourhood. But if the ions do not follow the electric force, and the existence of a negative force implies that some of them at any rate do not, we have no right to assume that the potential of the wire is the same as that of the gas. In some simple cases it is evident that it would not be so. Thus suppose the wire were exposed to a stream of cathode rays, and that there were no positive ions in its neighbourhood, then it is evident that the wire would acquire the potential of the cathode from which the rays started and not that of the gas around the wire.

For these reasons I felt that the existence of a negative force could not be established by means of wire electrodes, and I adopted an entirely different method of measuring the electric force along the discharge-tube. The principle of this method is as follows : Imagine a very fine pencil of cathode rays, travelling at right angles to the line joining the cathode and anode, to pass through the discharge-tube. As it crosses the discharge at any place it will be acted upon by the electric force at the point of the discharge, and will be deflected by an amount proportional to the electric force. The deflexion will be from the cathode of the discharge-tube if the force is positive, towards it if the force is negative. If very small pencils of cathode rays are used the disturbance of the electric field in the discharge-tube due to the negative charge on the rays is quite insignificant, and there is none of that distortion of the striations which, to a greater or less extent, always occur when exploring metallic electrodes are used.

The arrangement by which this principle is carried out in practice is shown in Fig. 2. The cathode and anode are fastened together by a piece of glass-rod and fastened to a float, floating on the top of a mercury column. By raising or lowering the column the anode and cathode can be moved up and down the discharge-tube. This arrangement is the same as that used with the wire detectors and shown in Fig. 3. The wires a b (Fig. 3) were replaced by cathode rays generated in the side tube S (Fig. 4) by a small induction-coil :

the cathode C is at the end of the tube, the anode is the metal plug A connected with the earth ; a very fine hole was bored in this plug and through it a pencil of rays passed across the discharge and then entered the side tube T.   In this tube there was a screen W, covered by a phosphorescent substance, in some cases willemite ; in others the screen was a zinc sulphide one procured from Mr. Glew.   The place of impact of the cathode rays against the screen is marked by a luminous spot, and by measuring with a cathetometer the deflexion of this spot the magnitude and direction of the electric force acting on the cathode rays as they pass across the discharge-tube can be determined.   Tinfoil was wrapped round the outside of the discharge-tube to neutralize the effect of electric charges on the glass walls of the tube.   The use of cathode rays not only avoids the disturbance due to the presence of the wires, but inasmuch as the cathode rays are negatively electrified particles it enables us to measure the effect
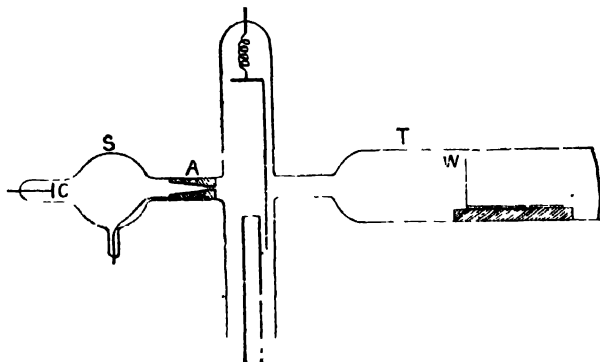
FIG. 4.

of the field on such particles, and as it is the corpuscles which carry practically all the current in the discharge, the method enables us to observe in a very direct way the most important factor in the discharge.

The method is, however, limited to the case where the pressure in the discharge-tube is low, as it is only at low pressures that the cathode rays produce a well-defined spot on the screen.

Observations made with this method showed unmistakably the existence of negative forces in certain parts of the discharge, and in fact the distribution of electric force along the tube as determined by this method agreed remarkably well with that determined by the method of the exploring wire.   When the discharge was striated it was generally found that where the cathode rays passed underneath a striation, i.e. on the cathode side of the bright part of the striation, there was a small deflexion of the cathode rays towards the cathode

of the discharge-tube, showing that in this part of the discharge the electric force is negative, while when the path of the cathode rays passed through the bright part of a striation there was a large deflexion of the cathode rays from the cathode of the discharge-tube, showing that in this part of the discharge the electric force was strongly positive. The change from the small negative deflexion to the strong positive one was exceedingly abrupt, so much so that when the anode and cathode were moving downwards, owing to the sinking of the float supporting them, and one striation after another was thus being brought across the path of the cathode rays, the phosphorescent spot moved as abruptly as if it had been struck by a blow when the bright head of a striation crossed its path. At the low pressures at which these observations are made the potential-difference between the electrodes when the current is large enough to produce striations is exceedingly small, often not exceeding 60 or 70 volts. Under these circumstances the negative forces although unmistakable are small : when, however, the current through the tube is reduced until the discharge is no longer striated, the potential-difference between the electrodes is very much increased, and now large negative forces can be observed in the neighbourhood of the anode. Sometimes the region in which the force is negative extends a considerable distance from the anode : in one case I observed a negative force for two-thirds of the distance from the anode to the cathode.

As the corpuscles in the cathode rays have an exceedingly small mass they are able to follow very rapid variations in the electric field ; by means of them we can observe the gradual establishment of the steady state of the discharge and the change in the direction of the electric force at certain places from positive to negative. Thus suppose the steady current through the tube is small and the potential-difference is considerable, and that the pencil of cathode rays is passing through the discharge near the anode, then if we watch the behaviour of the phosphorescent spot in the interval immediately following the application of the potential-difference to the tube, we shall find that when the current first starts through the tube the spot is repelled from the cathode, showing that at this stage the electric force is positive throughout the tube. This repulsion of the cathode rays is however only momentary : the spot jumps back, and after a very short interval the spot is *attracted* towards the cathode, showing that the force in this region is now negative. Thus during this interval the ions in the gas and those clinging to the walls of the tube have rearranged themselves in such a way as to reverse the force in the field. This momentary deflexion is much more perceptible near the anode than some distance away from it ; the rearrangement seems to spread from the cathode, and to be established so rapidly close to that electrode that there is no time to observe it, while as we travel away from the cathode the steady state

is reached after longer and longer intervals, and there is time to observe the initial distribution of the electric field.

We see that the result of the experiments with the cathode rays is to confirm the indications of the wire detector, even when the main current is travelling against the electric force. That the wires in this case should indicate the potential is very remarkable, and must be due I think to the presence in the discharge of slowly moving ions in addition to the swiftly moving ones which carry the main portion of the current, having acquired in other parts of the field sufficient impetus to carry them for some distance against an opposing electric force. The slowly moving ions would be produced by the collisions of the quick ones, and those produced near the tips of the wire electrodes would follow the lines of electric force near the wire and equalize the potentials between the wire and the gas.

The great change in the electric force which occurs at the bright fronts of the striations shows that in these regions we have a great accumulation of negative electricity, while the distribution of the electric force in other parts of the striations and in the dark parts between two striations shows that in those regions there is a slight excess of positive electricity. The magnitude of the charges in the electric force is shown by the following numbers, which indicate the electric force in volts per centimetre at different parts of the striation. x in the following table is the distance in millimetres from the bright head of the striation : x is taken positive when measured towards the anode, negative towards the cathode, thus $x = -1$ denotes a place 1 millimetre from the bright head of the striation on the cathode side. X is the electric force in volts per centimetre at x. The gas was hydrogen at a low pressure.

x	X
$-$ ·5	$-$ 9
$+$ ·5	$+$ 67
$+$ 1·5	$+$ 33
$+$ 3·5	$+$ 30
$+$ 7	$+$ 10
$+$ 9	$-$ 10

The last reading was at a point just in front of a second striation.

The distance between the bright heads of successive striations was 9 mm. and the thickness of the dark space 2 mm.

From the preceding table we see that in the space of 1 mm. at the head of a striation we have a change in the electric force of 76 volts per cm. By means of the equation

$$\frac{d\,X}{d\,x} = 4\,\pi\,\rho$$

we see that the density of the negative electricity at the head of the striation is about $\frac{1}{5}$ of an electrostatic unit per c.c. The density of the positive electricity in the other portions is very much less than this. With Wehnelt electrodes there is frequently only a small potential-difference between corresponding points in adjacent striations : in some cases this difference was only 2·7 volts.

The changes in the electric force are much more abrupt at low pressures than at high ones ; though there is always a large increase in the force at the bright head of the striation. I have not observed the existence of the negative forces when the pressure was more than a fraction of a millimetre of mercury.

I have found other cases in which the negative forces are even more pronounced than those I have already considered ; perhaps the most striking of these is one where the anode and cathode are connected together and with earth by stout metallic connexions, so that the two are at the same potential, and therefore the average negative force between them is as great as the average positive force. The anode is perforated by a very fine hole, and through this hole a stream of Canal rays, i.e. positively electrified particles, passes into the tube : this produces when the pressure is suitable a fully developed discharge, with striations, Faraday dark space, a well-developed negative glow and dark space ; and in spite of the anode and cathode being at the same potential there is in this case the normal cathode fall of about 300 volts at the cathode : the negative forces in a tube of this kind must be very considerable, as they have to balance the cathode fall.

The heaping up of the negative electricity at the head of the striations seems to me to be the most important factor in the production of striations.

This concentration of the negative electricity at regular intervals along the discharge may be explained as follows. Consider a stream of negative corpuscles projected from the neighbourhood of the cathode with considerable velocity : they will collide against the molecules of the gas, and thereby lose velocity : if the electric field acting on them is not sufficiently intense to restore the velocity lost by the collisions, the corpuscles will lose velocity as they travel through the gas, thus the corpuscles in the rear will gain on those in front, and therefore the density of the corpuscles and therefore of the negative electricity will be greater in the front, and by the equation $\dfrac{d\,\mathrm{X}}{d\,x} = 4\,\pi\,\rho$, when X is the electric force, x the distance from the cathode, and ρ the density of the electricity, the electric force will increase rapidly in consequence of this concentration. This increase in the force will increase the velocity of the particles in front. If the increase in velocity is not sufficient to make the corpuscles ionize the gas by collision, the congestion will be relieved by the gradually increasing velocity of the corpuscles in front, and there will be no periodicity either in the density of the electricity or the electric force.

If, however, the force increases so that the corpuscles produce ions by collision quite a different state of affairs will occur ; suppose that when the corpuscles get to a place P, their velocity is sufficient to produce ionization.   On the anode side of P positive and negative ions will be produced, the positive ones will crowd towards P, the negative ones will move away from it ; the consequence will be that there will be an excess of positive electrification on the anode side of P : now positive electrification implies a diminution in the electric force as we move towards the anode, thus the electric force will fall. When it has fallen below the value required for ionization the negative electricity will as before begin to accumulate in the front of the stream, and the electric force will again increase to the value required for ionization when the process will be repeated.   We shall in this way get a periodicity in the electric force such as is observed in the striated discharge.   Thus on this view the concave side of the bright head of the striation acts as a cathode, the corresponding anode being the convex side of the bright head of the adjacent striation on the anode side.   Between these two places we have a complete discharge, forming a unit by the combination of which the whole discharge is built up.   The ions which carry the current through any unit are for the most part manufactured in the units themselves, so that these units will behave, as Goldstein and Spottiswoode and Moulton have observed the striations to behave, as if they were to a considerable extent independent of each other.   The effect of pressure on the distance between the striations can easily be understood from this point of view, for the lower the pressure the greater will be the distance which particles projected with high velocity will travel before their velocity is destroyed.   Again, the variations in the electric field are due to the accumulation of electrical charges in the tube.   These accumulations may be regarded as electrified disks whose cross-section is that of the tube ; the distance from the disk at which these forces fall to a certain fraction of their maximum value will depend upon the diameter of the disk ; the larger the diameter the greater this distance, so that when the diameter of the tube is small the fluctuations in the intensity of the electric force will be much more rapid than when it is large, and thus we should expect the striations to be much nearer together in a narrow tube than in a wide one.

To explain the variations in the luminosity which accompany these fluctuations in the electric field we must consider the variation in the kinetic energy possessed by the positive ions when they recombine.   The recombination of ions does not in general seem to be accompanied by luminosity, unless the ions possess a definite amount of kinetic energy.   We certainly can have a gas with great electrical conductivity, and in which a large number of ions are recombining without any visible luminosity ; it seems as if the ions must have a definite amount of kinetic energy for visible light to be developed on their recombination.   Now in the space between two striations the

electric field in the part near the cathode side of the bright head of a striation—the dark part—is weak ; here the ions have not got the minimum amount of energy requisite for them to be luminous when they recombine ; in the bright part of the striation the electric field is strong, and here the ions get sufficient kinetic energy to enable them to give out light when they combine. If the energy required for an ion to give out visible light is greater for light at the blue end of the spectrum than at the red, we might get blue light at one part of the striation, red at another, an effect often observed when we have a mixture of mercury vapour and hydrogen in the tube ; a similar separation of the spectra of the two gases in a striation might also be produced if one of the gases were more easily ionized than the other.

I wish to thank my assistant, Mr. Everett, for the assistance he has given me in these investigations.

Friday, April 23, 1909.

THE RIGHT HON. LORD RAYLEIGH, O.M. P.C. M.A. D.C.L.
LL.D. F.R.S., in the Chair.

ALEXANDER SIEMENS, ESQ., M. INST. C.E., *M.R.I.*

Tantalum and its Industrial Applications.

WHEN the announcement was made in the year 1878 that "the division of the electric light had been successfully accomplished," many people believed that the days of lighting by gas had come to an end, and acted accordingly, much to their own disadvantage : for the competition of the glow-lamp served only to stimulate its rival to new life.

Burners of improved construction, regenerative burners, and finally gas mantles helped to restore to gas the ground it had lost, and until a short time ago even threatened to check the spreading of electric lighting.

Not only this growing competition of gas, but the universal necessity of cheapening the production of commodities that are for general use, forced electrical engineers to study in all its aspects the question of improving the efficiency of electric lighting.

As a guide in their researches they had the well-known principle that the illuminating power of a solid body increases at a much greater ratio than its temperature, or, in other words, that with the increase of temperature a greater percentage of the energy expended for heating the body is converted into light.

There is plenty of room for improvement ; for even the most economical source of light, the electric arc lamp, converts only about one per cent. of the energy of the electric current flowing through it, into light, the rest appearing as heat, so that in reality all methods of lighting devised by men are, to a much greater extent, methods of heating.

The first successful incandescent lamp consisted of a carbon filament ; and for a long time carbon appeared to be the only suitable substance, although the temperature to which such a filament can be raised is limited to about 1600° C., as above this point the carbon begins to disintegrate rapidly.

At this temperature the lamp consumes from three to three and a half watts per candle-power, while any attempt to produce light more economically by raising the temperature of the filament results only

in shortening its life, and destroying thereby its power of competing with gas lighting.

An improvement on this result was introduced by Prof. Nernst, of Göttingen, who suggested, as the source of light, refractory earths, similar in character to those used for gas mantles, which, however, conduct electricity only when they are hot.

Lamps constructed on Prof. Nernst's principle have, therefore, to be fitted with contrivances for heating their filaments when starting, which complicate the construction of the lamp.

Another step forward was made by the invention of the osmium lamp, which is produced in a somewhat similar manner to the carbon lamp, by squirting a plastic mixture of metallic oxide and a reducing agent into the shape of a filament, which is gradually heated in a glass bulb by the passage of an electric current, while the bulb is being exhausted by an air pump, or an equivalent device.

As far as utilisation of energy goes, these lamps are a great improvement on carbon lamps, but their filaments are very brittle ; and the total production of osmium per year is only about 8 kg. for the whole world, of which 5 kg. are wanted for medical purposes.

In January 1905 Dr. W. von Bolton, the head of the chemical laboratory of the firm of Siemens and Halske, announced in a lecture to the Elektrotechnische Verein of Berlin that he had succeeded in producing pure tantalum, and his discourse was followed by Dr. O. Feuerlein, describing how tantalum had been utilised for filaments in the lamp works of the firm.

These discourses presented the result of long years of research work, based on the general principle already alluded to, that that filament would give the best economical results which could be maintained for the longest time at the highest temperature.

The number of substances capable of conducting electricity and of sustaining such high temperatures is very limited, and platinum, the most refractory of the well-known metals, had been tried and found wanting.

It became, therefore, necessary to start the research by devising methods for producing the rare metals in a commercially possible manner, and then try one after the other as filaments of incandescent lamps.

While working on these lines, Dr. von Bolton succeeded, in the first instance, in producing a vanadium filament by heating a mixture of vanadium pentoxide and paraffin to 1700° C., and thereby producing sticks of vanadium trioxide, which in their turn were heated by electric currents in a glass bulb exhausted by an air-pump, and so converted into metallic filaments.

As it was found that vanadium melts at about 1680° C., such filaments were no improvement on carbon filaments ; and the next substance to be investigated was niobium, which belongs to the same group of elements, but has nearly double the atomic weight.

Treated in a similar manner, the niobium filament gave somewhat better results, but still its melting-point, estimated at 1950° C., was too low for practical purposes.

In this connection it should not be forgotten that, at a temperature considerably below their melting-point, all these metals begin either to soften or to disintegrate, so that their "working" temperature is not identical with their melting temperature.

Turning his attention to tantalum, which has an atomic weight of 181, Dr. von Bolton experimented with the black metallic powder produced by the method of Berzelius. and Rose, and found that it could be rolled into a fairly coherent mass in the form of ribbons.

Alternative experiments, conducted on the lines by which vanadium and niobium had been obtained, resulted in the production of pure tantalum in the form of a metallic button, which was found to be tough and malleable like steel.

These and other qualities convinced Dr. von Bolton that nobody before him had handled pure tantalum, although Berzelius had first obtained the metal by a chemical process in 1824, and later Moissan succeeded, in 1902, in producing it in his electric furnace.

The latter describes tantalum as a hard brittle metal of the specific gravity of $12 \cdot 8$ and a non-conductor of electricity, but he adds that the substance obtained by him contained about a half per cent. of carbon.

Considering the high atomic weight of tantalum, this admixture of carbon evidently exercises a great influence on the physical qualities of tantalum, and explains the differences between the observations of Dr. von Bolton and those of his predecessors.

In nature ores containing tantalum are found in many places, principally in Scandinavia, North America, South-west Africa, and Western Australia.

A specimen of columbite from South Dakota and another of tantalite from Western Australia are exhibited.

The columbite contains from 10 to 40 per cent. of tantalum pentoxide (Ta_2O_5), and a good deal of niobium combined with iron and manganese in various proportions.

As the separation of tantalum and niobium is somewhat troublesome, it is preferable to utilise the tantalite, which consists almost entirely of iron and manganese combined with tantalum pentoxide.

From these ores tantalum is separated in the form of a fluoride in combination with potassium ($K_2Ta Fl_7$), and subsequently reduced by metallic potassium to the black powder already mentioned, which, however, still contains some oxide and some hydrogen.

In order further to purify the product, the powder is pressed into the form of small cylinders (one of which is on the table), which are melted in a vacuum by an electric current under certain precautions into small buttons of pure tantalum such as are exhibited.

Since the production of tantalum has been carried out on a com-

mercial scale, it has been possible to improve many details of the process, so that the tantalum produced by it at the present time is even purer than that shown in 1905 at the discourse of Dr. von Bolton and Dr. Feuerlein.

Some specimens of this latest tantalum have been submitted to Sir James Dewar, who has very kindly made experiments with reference to its specific heat and to its thermal conductivity.

He ascertained the specific heat by plunging small spheres of tantalum, which had been heated to the temperature of boiling water, into water of 14° C., then transferring them to melting carbonic acid ($-78°$ C.), and finally to liquid air ($-183°$ C.), and as an average of several experiments the specific heat was found to be between

$$
\begin{array}{rcl}
100° \text{ C. and} & 14° \text{ C.} & = 0\cdot033 \\
14° \text{ C. ,,} & -78° \text{ C.} & = 0\cdot032 \\
-78° \text{ C. ,,} & -183° \text{ C.} & = 0\cdot028
\end{array}
$$

while Dr. von Bolton in 1905 gave the specific heat as $0\cdot0363$.

Multiplying these results by the atomic weight (181) it will be seen that Dr. von Bolton's value ($6\cdot57$) is slightly higher, and Sir James Dewar's value ($5\cdot97$) lower than $6\cdot4$, which, according to Dulong and Pettit is the atomic specific heat.

By the kindness of Sir James, his experiment for showing the relative thermal conductivity of iron, copper and tantalum can be repeated here by dropping three short rods, made of these metals, in liquid air, while their tops, above the cardboard cover, are exposed to the air of the room.

In a short time the moisture of the air condenses on the rods and freezes to a distance, which depends on the conductivity of each metal.

The results of Sir James Dewar's experiments prove tantalum to have about three-quarters the conductivity of iron, and about one-eighth the conductivity of copper.

At ordinary temperatures, say below 300° C., pure tantalum resists the action of all acids, except fluoric acid, of all alkalies, and of moisture, so that it is an ideal material for chemical apparatus which do not require high temperatures, and for any implements which, when made of steel, are liable to rust.

It has already been stated that pure tantalum is rough and malleable, so that it can be hammered out into thin sheets or drawn into fine wire, the diameter of the filament wire being $0\cdot03$ mm. or about one-eight-hundredth of an inch ; all the same, it is elastic and as hard as soft steel, and has a tensile strength of 93 kg. per square mm., which is equal to 57 tons per square inch.

This means that the filament wire is capable of supporting about 80 grammes, or $2\cdot8$ ounces, as can be shown by actual experiment.

Tantalum sheet can be stamped into various shapes, and out of

bars of tantalum springs can be bent, as the specimens on the table show.

Another use made of tantalum is as material for writing pens, manufactured in the usual way.

When it was first offered for this purpose, it was found that the material could not pass the test prescribed for pens made of steel.

These are pressed by a weight of 180 grammes on writing paper, which is moving at the same speed as ordinary writing, and while 10 km. (6¼ miles) of paper are passing, the loss by abrasion must not exceed 0·7 mg. (0·01 grains).

At first the tantalum pens lost more than double the permitted weight, but it was found that slightly oxidising the surface of the pens hardens them so much, that they only lose 0·8 mg. by the 10 km. test.

By weight this is still more than permitted for steel pens, but having regard to the specific weights of the two substances, the actual volumetric abrasion of the tantalum pen is the lesser of the two.

Although only the surface of the pens had been oxidised, it was found that the rate of abrasion remained the same for the whole length of 10 km., when it was expected that this rate would increase materially after the skin of oxide had been ground off.

Advantage was taken of this circumstance when an inquiry was received from India whether it would be possible to manufacture cataract knives for oculists out of tantalum.

The qualities demanded of such a knife are that its blade should be—

1. Intensely hard, so as to be able to acquire a very sharp edge of great smoothness, and to retain this fine edge for a long time.

2. Very tough without any tendency to bend.

3. Chemically and mechanically stable, so that it can be easily sterilised and that it is not liable to rust.

4. Capable of acquiring a high polish.

Manufacturing such a blade out of pure tantalum and slightly oxidising it, before polishing it, appears to fulfil these stringent conditions, but as the knife which is on the table has not yet been actually tried for an operation, it can only serve to demonstrate the similarity of tantalum to steel for such purposes.

Another field for the application of tantalum may be found in the supply of dental instruments, owing to its immunity from chemical changes, but beyond showing two cases of such appliances, there is no necessity to go further into details.

While possessing all these qualities of a true metal, tantalum has some others which rather limit its usefulness.

When heated to a dull red it absorbs gases greedily, especially hydrogen and nitrogen, and by combining with them it loses its tensile strength and becomes brittle.

Here are three pieces of tantalum wire taken from the same coil ;

one of them has been heated in an atmosphere of nitrogen, the other in hydrogen, and the third has not been interfered with. The consequence is that the latter has retained its strength, while the former have become brittle and useless.

On heating tantalum in air, it shows first a yellow and then a blue tint like steel, but when the heating is continued it burns to pentoxide.

The black powder and thin wires can even be lighted by applying a match to them, as the experiment shows.

Its melting-point, in vacuo, lies between 2250° C. and 2300° Celsius, which makes it particularly suitable for electrodes in vacuum-tubes, especially as it does not disintegrate—for example, Ta electrodes are extensively used in Roentgen tubes—and its specific weight is 16·6.

Turning now to the electrical qualities of tantalum, its specific resistance was stated by Dr. von Bolton, in 1905, to be on the average 0·165, with a temperature coefficient of 3 per cent. between 0° and 100° Celsius.

Further experiments conducted by Dr. Pirani in the laboratory of Siemens and Halske revealed the fact that wires of various thicknesses varied in their specific resistance from 0·173 to 0·188; but after they had been heated to 1900° Celsius in a high vacuum for from 100 to 200 hours, they all possessed the same specific resistance, viz.: 0·146, and their temperature coefficient between 0° and 100° Celsius had risen to 0·33 per cent.

As a temperature of the tantalum filament, when consuming 1·5 watt per candle-power, is about 1850° C., and its resistance about six times its resistance at 100° C., the temperature coefficient between 100° and 1850° C. may be taken, on the average, as 0·29 per cent.

No doubt the difference between these results is caused by alterations in the structure of the wires during their manufacture, and the heating in vacuo served a similar purpose to the annealing of steel, so that Dr. Pirani's results published in 1907 may be taken as standards.

At present, the most important industrial application of tantalum is its use for the filaments of incandescent lamps, which may be said to date from July 1903, when Dr. Feuerlein had succeeded in producing a tantalum wire one-twentieth of a millimetre in diameter. Of this wire he made a glow lamp with a filament 54 mm. long, using a current of 9 volts 0·58 amps., and giving a light of 3·5 candles (Hefner), at the rate of 1·5 watt per candle power.

A simple calculation shows that for a current of 110 volts, 660 mm. of the same wire would be required giving at the same rate of consumption of energy a light of 43 candles.

In carbon lamps for 220 volts the length of filament is only 400 mm., and the filaments remain hard until they disintegrate. Tantalum filaments, like other metallic filaments, soften, however, to such a degree that they cannot be used in the same shape as carbon filaments.

After trying various methods of housing the long Ta filament in a glass bulb of approximately the same dimensions as the carbon glow lamps, the present form was arrived at during the year 1904.   In this lamp, which was adopted as standard, the length of the filament was 650 mm., its diameter 0·05 mm., and its weight 0·022 grammes, so that about 45,000 of these lamps contain 1 kg. of Ta.

Since then these dimensions have been modified to a certain extent, for instance the diameter of the filament is now only 0·03 mm., but the external shape has not been altered.

It was soon found that after burning a short time the filament underwent certain structural changes and lost its great tensile strength. Examination under a microscope revealed the fact that in about 1000 hours the smooth cylindrical filament shows signs of capillary contraction, as if the cylinder was going to break up into a series of drops, and the surface, from being dull, commences to glitter.   This contraction of the filament after being heated is readily recognised by comparing a new lamp with an old one.   On the stars of the new lamp the filament hangs loosely, while in the old lamp the filament is evidently in tension.

The characteristic difference between carbon filaments and tantalum filaments is shown by a diagram representing the influence of temperature on the electric resistance of the two filaments in proportion to each other.

In order to have the differences at once shown in per cents., the normal pressure and the normal resistance of both filaments, when giving the light of 1 candle for 1·5 watt, is marked as 100, and it is immediately seen that the resistance of Ta alters directly and that of carbon inversely as the temperature.   Owing to this quality, a Ta filament is better able to resist overheating than a carbon filament, as the following experiment shows, where two lamps, one Ta and one C, burning normally at 110 volts with 1·5 watt per candle power, are gradually exposed to higher voltages.   The C lamp breaks while the Ta lamp stands up to 200 volts, the highest voltage available to-night. Of course its useful life will be shorter than at its normal voltage.

As stated at the beginning of the discourse, the primary object of all the research was to find a filament more economical in the consumption of electrical energy than the C filament, and the following experiments will show that the Ta filament is, in this respect, a great improvement on the C filament.

To begin with, a comparison can be made by burning a Ta and a C lamp under water, each being immersed in a vessel containing the same quantity of water.

Owing to the C lamp requiring more energy to give the same light as the Ta lamp, the temperature of the water in the C vessel rises quicker than in the other vessel.

Another way of showing the difference is by measuring the current taken by each of the two lamps when giving approximately the same

light, or by sending the same current through both lamps in series and noting the difference in candle power.

In conclusion, two interesting qualities of Ta should be noted—

The first is that when a Ta filament is heated in a high vacuum it will expel any oxygen that has combined with it. It is possible to detect whether a filament contains any oxide by very gradually heating it up, when the parts containing oxide will appear brighter than those consisting of pure Ta, owing to the greater electrical resistance of the oxide.

These lamps have been purposely exposed to the air while they were being exhausted and have become " spotty " in consequence, but if they are raised a little above their proper voltage and left burning for a few minutes, their filaments become quite uniform by the expulsion of the oxygen.

The second is that Ta will act as a rectifier when used in an electrolyte, that is to say, it will allow of the passage of the positive current only in one direction. In the apparatus shown the positive current passes through the lamp to a Ta anode, thence to a Pt cathode, but in a very short time the Ta anode covers itself with a film of oxide which stops the current. When the current is reversed the lamp lights again and continues to burn. When an alternate current is connected to the lamp it will also continue to burn, but with reduced light.

All these experiments are intended to show the remarkable qualities of this material, and when they are fully appreciated and its limitations are properly understood, there appears to be a great field open to tantalum and its industrial applications.

[A. S.]

Friday, May 28, 1909.

His Grace The Duke of Northumberland, K.G. P.C.
D.C.L. Sc.D. F.R.S., President, in the Chair.

J. Emerson Reynolds, Esq., M.D. Sc.D. F.R S. *M.R.I.*

*Recent Advances in our Knowledge of Silicon and of its Relations
to Organised Structures.*

I HAVE placed on the table before you a magnificent natural
crystal of the colourless mineral *quartz*, which is the property of the
Royal Institution. This is the oxide—dioxide—of the element Silicon,
about which I have the honour to address you this evening. This
oxide of Silicon is—as you are doubtless well aware—commonly called
Silica, and is met with in Nature in many conditions, either colour-
less as in this "rock crystal" or coloured in the black quartz, in
common topaz and amethyst, and uncrystalline in agate and flint.

Not only is Silicon widely diffused in Nature in the many forms of
its oxide, but it also constitutes between one-third and one-fourth of
the original and non-sedimentary rocks—of which the solid crust of
the earth largely consists—in these cases being chemically combined
with Oxygen and various metals forming natural *Silicates.* In this
diagram we have a necessarily very rough estimate of the relative
proportions in which the chief constituents are present.

THE EARTH'S CRUST.

Approximate average Composition of non-sedimentary Rocks.

Oxygen	..	..	about 47 per cent.
Silicon	..	..	„ 28 „
Aluminium	..	..	„ 8 „
Iron	..	..	„ 7 „
Calcium and Magnesium		..	„ 6 „
Alkali Metals		..	„ 4 „

The crust of the earth is in fact a vast assemblage of silicon com-
pounds, and the products of their disintegration under the influence of
water and other agents produces the various forms of clay, sand and
chalk which constitute so large a portion of the earth's surface.

The solid crust of the earth is actually known to us for but a very
few miles down—thirty at most—our deepest mines being mere
scratchings on its surface ; but, so far as known, practically all its
constituents are fully oxidised, and this is probably true at much
greater depths. During æons past oxygen has been absorbed as the

earth cooled down, and the product is the crust on which we live.* It is probable that the proportion of oxygen diminishes away from the surface until it disappears almost wholly. What of the deeper depths ? Are the comparatively light elements arranged more or less in the order of density ? Are we to suppose that silicon and some carbon, aluminium, calcium, the elements chiefly comprising the crust, are those nearer the surface, and iron, copper, and the heavier metals nearer the centre ?

Until recently we knew little more than that the earth is some 8000 miles in diameter ; that its mean density is 5·6–5·7, and that its relatively thin outer skin, or crust, has approximately the composition assigned to it in the diagram. By a very skilful use of earthquake observations, the eminent geologist, Mr. Richard D. Oldham has, however, lately† given us something like a glimpse within the ball, and concludes from his observations that about five-sixths of the earth's radius includes fairly *homogeneous* material and that the remaining sixth at the centre consists of substances of much higher density. Assuming this to be even roughly true, we conclude that silicon forms probably as great a proportion of this large mass of the earth—whether in the free state or in the forms of silicides—as it does of the crust.

Having thus magnified the office of the important element of which I wish to speak to you, I shall pass to my next point which is how the element can be separated from quartz, or other forms of the oxide, for it is never met with unless combined with oxygen in any of the rocks known to us.

I have already mentioned that quartz is a dioxide of the element —in fact it is the only known oxide—hence if we remove this oxygen we should obtain free silicon. This is not a very difficult matter as it is only necessary to heat a mixture of finely powdered quartz with just the right proportion of metallic magnesium. The metal combines with the oxygen of the quartz, and forms therewith an oxide of magnesium, while silicon remains. If the material be heated in a glass vessel the moment of actual reduction is marked by a bright glow which proceeds throughout the mass. When the product is thrown into diluted acid the magnesium oxide is dissolved and nearly pure silicon is obtained as a soft dark brown powder which is not soluble in the acid. This is not crystalline, but if it be heated in an electric furnace it fuses and on cooling forms the dark crystalline substance on the table, which, as you see, resembles pretty closely the graphitic form of carbon, though its density is rather greater. (2·6, graphite being 2 ·5.)

* An interesting calculation has been made by Mr. Gerald Stoney, from which it appears that a stratum only 9 feet in depth of the surface of the earth contains as much oxygen as the whole atmosphere. See Phil. Mag., 1899, p. 566.
† R. D. Oldham, F.G.S., "Constitution of the Interior of the Earth." Quarterly Journal of the Geological Society, vol. lxii. (1906) pp. 456–475.

SILICON ANALOGUES OF CARBON COMPOUNDS.

The points of physical resemblance between silicon and carbon are of small importance compared with the much deeper rooted resemblance in chemical habits which exists between the two elements. This is expressed in the periodic table of the elements as in the following diagram :—

Na=23, Mg=24, Al=27, **Si**=28, P=31, S=32, Cl=35·5
Li = 7, Be = 9, B=11, **C**=12, N=14, O=16, F=19

where silicon is represented as the middle term of a period of seven elements of increasing atomic weights, just as carbon is the middle term of the previous period. The fact is these two electro-negative or non-metallic elements play leading parts in the great drama of nature, silicon dominating that which has to do with dead matter, while carbon is the great organ-building and maintaining element of all living things. While each carries on the work to which it is best suited under existing terrestrial conditions, they both go about it in somewhat similar ways and each one shows tendencies to overstep the border line and perform the other's part. This tendency is for various reasons much more marked in the case of carbon, but I hope to show you presently that silicon is by no means out of touch with living things, and further that it exhibits capacities which render it a potential element of life under other conditions of our planet, but more especially at a much higher level of temperature.

I do not propose to dwell in much detail on the remarkable parallelism of some silicon and carbon compounds, but must refer shortly to a few of them, and the oxides naturally come first.

I have just stated that we know with certainty only one oxide of silicon, the dioxide SiO_2. This is analogous to the highest oxide of carbon—the well-known CO_2 which plays so important a part in the lives of animals and plants. This familiar carbon compound is a gas under ordinary conditions, but here is some of it in the form of snow. Alongside of this is a vessel containing some finely divided SiO_2 or silica. They are rather like in appearance but they differ greatly in volatility. The CO_2 snow speedily resumes the gaseous state at ordinary temperature, but silica requires a very high temperature indeed even for fusion, however when heated in an electric furnace, the oxide can not only be fused but volatilized. In the fused state it can be fashioned into various shapes and affords most convenient vessels for many purposes, as they are not liable to crack on sudden heating or cooling, and are not attacked by any acid except hydrofluoric acid.

As the difference between the atomic weights of the elements carbon and silicon is only 16 units, silicon dioxide should not differ in volatility nearly so much as it does from carbon dioxide. This and

other considerations lead us to the conclusion that silica as we know it is a molecularly condensed substance represented by the expression $(SiO_2)_n$, where the value of n is probably at least $=6$.

Before leaving the consideration of the simple oxide, I should like to show you the effect of radium emanations on a disc of colourless quartz. This disc has been exposed by Sir William Huggins to radium for a considerable time, and the brownish discoloration about the centre of it is due to the action of the rays. Whether the latter reduce a portion of the oxide and separate a minute film of brown silicon, or merely attack some trace of impurity in the quartz is not yet known. I have to thank Sir William Huggins for allowing me to show you this interesting specimen.

The chemical analogies of CO_2 and SiO_2 are very close in many respects, for both act as acid anhydrides and combine with metallic oxides and form similar salts. On the one hand we obtain the well-known carbonates, such as common soda crystals, and on the other *silicates*, such as sodium *silicate*. I need scarcely remind you that ordinary window and bottle glass are mixtures of silicates of such metals as calcium and sodium.

When a soluble carbonate is treated with any moderately strong acid CO_2 gas is evolved ; but when a soluble silicate such as Na_2SiO_3 is similarly treated no gas is evolved but a gelatinous substance separates. Now this consists for the most part of the feeble acid H_2SiO_3, which parts with the elements of water gradually, if exposed to air, and affords various lower hydrates, one of the most beautiful being that which we meet with in Nature as the precious *opal*.
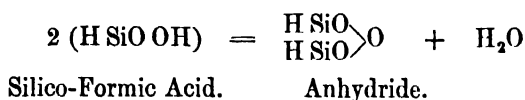
Chloride and bromide of silicon are easily obtained by heating the free elements in the respective halogens, and precisely correspond in composition to the analogous carbon compounds, but, unlike the latter, are intensely reactive to water, and in so far resemble the chloride and bromide of a metal.

If, however, hydrochloric acid gas, instead of chlorine, be passed over heated silicon a very volatile liquid is obtained which is similar in composition to ordinary carbon *chloroform* :—

| Ordinary Chloroform | ... | ... | $CHCl_3$ |
| Silicon Chloroform | ... | ... | $SiHCl_3$ |

Silicon chloroform has no anæsthetic effects for a reason you will easily appreciate, when I compare the action of water on the two substances. Under ordinary conditions carbon chloroform is not affected by moisture, hence its vapour can be taken into the lungs unchanged and passes into the system producing its characteristic effects. Silicon chloroform on the other hand is instantly destroyed by moisture, producing free acid, therefore it cannot be inhaled. Nevertheless, the products of the action of water upon it at ordinary temperature are very similar to those which can be obtained by the

prolonged action of water on ordinary chloroform at *high* tempera-
tures. The latter can afford formic acid along with hydrochloric acid.
Silicon chloroform affords precisely similar products at ordinary tem-
peratures, but the soluble silico-formic acid immediately changes into
the anhydride, and that is the white insoluble substance which has
separated in the tube before you. This change may be represented
thus :—

$$2 \text{ (H SiO OH)} \quad = \quad \begin{matrix} \text{H SiO} \\ \text{H SiO} \end{matrix} \Big\rangle \text{O} \quad + \quad \text{H}_2\text{O}$$

Silico-Formic Acid.   Anhydride.

Again, both silicon and carbon form gaseous compounds with
hydrogen of similar composition : —

$$\text{CH}_4 \text{ and } \text{SiH}_4$$

Neither of these hydrides can be obtained by direct union of the
respective elements, though they are easily obtained by indirect
means, with the details of which I need not trouble you. Both are
colourless gases as you see. The carbon hydride, or marsh gas, is
combustible, but requires to have its temperature raised considerably
before it takes fire in air, and its flame is only slightly luminous. It
produces on complete oxidation water vapour and carbon dioxide gas.
The analogous silicon hydride takes fire much more easily in air, and
when not quite pure is even spontaneously combustible under
ordinary conditions, and it burns producing water vapour and solid
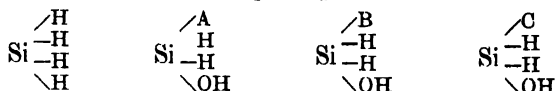silicon dioxide.

" SILICO-ORGANIC CHEMISTRY."

Now, just as marsh gas may be regarded as the starting point of
that great branch of science which is usually spoken of as Organic
Chemistry, so the analogous hydride of silicon is the primary com-
pound from which many substances which are often termed silico-
organic compounds can be derived by various means, and these were
discovered in the course of the classical researches of Friedel,
Crafts, Ladenburg and others.

I wish to avoid using many chemical formulæ, which probably
would convey but little meaning to some of those whom I address ;
it will suffice to merely indicate the *lines* on which investigations
have proceeded in this direction.

In the older work of Friedel, Crafts and Ladenburg, they
produced complex substances by the substitution of various radicles
(always carbon groups), for one atom of hydrogen in SiH_4, and
ultimately replaced another atom of hydrogen by the OH or hydroxyl
group. The substances so formed were silicon *alcohols* which may be

represented in the following manner—A, B and C, being used to indicate the different complex replacing radicles :—

$$\mathrm{Si} {\diagup\!\!\!\!\begin{array}{l}\mathrm{H}\\-\mathrm{H}\\-\mathrm{H}\\\diagdown\mathrm{H}\end{array}} \qquad \mathrm{Si} {\diagup\!\!\!\!\begin{array}{l}\mathrm{A}\\\mathrm{H}\\-\mathrm{H}\\\diagdown\mathrm{OH}\end{array}} \qquad \mathrm{Si} {\diagup\!\!\!\!\begin{array}{l}\mathrm{B}\\-\mathrm{H}\\-\mathrm{H}\\\diagdown\mathrm{OH}\end{array}} \qquad \mathrm{Si} {\diagup\!\!\!\!\begin{array}{l}\mathrm{C}\\-\mathrm{H}\\-\mathrm{H}\\\diagdown\mathrm{OH}\end{array}}$$

In this way silicon alcohols were built up which proved to be analogous to well-known carbon alcohols, and which afforded analogous acids, etc., on oxidation. These discoveries laid the foundations of a silico-organic chemistry and have been further extended in later years. For example, it has been found possible to pursue the analogy with known carbon compounds in the direction of replacing all the hydrogen in silicon hydride by different radicles, and these changes, which can be effected in successive stages, may be represented in harmony with those just given :—

$$\mathrm{Si} {\diagup\!\!\!\!\begin{array}{l}\mathrm{A}\\-\mathrm{H}\\-\mathrm{H}\\\diagdown\mathrm{OH}\end{array}} \qquad \mathrm{Si} {\diagup\!\!\!\!\begin{array}{l}\mathrm{A}\\-\mathrm{B}\\-\mathrm{H}\\\diagdown\mathrm{OH}\end{array}} \qquad \mathrm{Si} {\diagup\!\!\!\!\begin{array}{l}\mathrm{A}\\-\mathrm{B}\\-\mathrm{C}\\\diagdown\mathrm{OH}\end{array}}$$
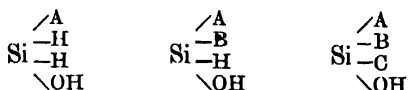
The two last of these are *asymmetric*, since all four radicles are different. Consequently they should exist in two isomeric modifications, if really analogous to known carbon compounds of the same order, and each form should be capable of acting differently on polarised light.* Dr. F. Stanley Kipping, who has specially investigated this kind of substitution with much success, finds that the analogy between these asymmetric silicon and carbon compounds is complete in regard to optical activity as to other general characters.

SILICON COMPOUNDS INCLUDING NITROGEN.

This was all good so far as it went, but some highly important information was still wanting. As you know well the various compounds including carbon and *nitrogen* play by far the most important parts in building up organised structures under the influence of vital energy, but in the silicon series we were almost wholly ignorant of the existence of such compounds until within recent years when I undertook to definitely investigate this branch of the subject.

All that was known at the period of which I speak was that silicon forms a white nitride of uncertain composition when strongly heated in an atmosphere of nitrogen gas ; and that when silicon chloride is brought in contact with ammonia and similar substances violent action occurs, but the nature of the products formed was not known owing to special practical difficulties in separating them.

The first step taken was to examine the action of silicon halides

* These changes are represented above as having been effected through the silicon alcohols in order to avoid complicating the general statement, other compounds have in fact been found more convenient for the purpose.

(i.e. chloride, bromide, etc.) on substances free from oxygen, but rich in nitrogen.   The earliest of these worked with were Thio-carbamides, but in all these cases the silicon halide merely united with the nitrogen compound as a whole, in some instances producing very curious substances of which the one with Allyl-thio-carbamide

$$(C_3H_5 . H_3N_2CS)_8 SiBr_4$$
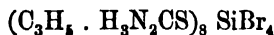
is a good example. This is a liquid which flows so slowly at ordinary temperature that it requires nearly a month in order to fall from the top of its containing tube and find its level at the bottom. Several similar substances have been obtained and examined and their products of decomposition studied, but they do not belong to the class of which I was really in search.

It would weary you to give the details of scientific prospecting which one has to go through in order to attain definite results in a new line of work like this, suffice it to say that success attended the efforts at last, and a finely crystallised and perfectly defined compound was obtained in which silicon is wholly in direct chemical combination with nitrogen, and a specimen of that substance I now show you. Its composition is represented by the expression

$$Si\ (NHPh)_4$$

where Ph stands for the phenyl group, and its name is Silico-phenylamide.

This substance when heated undergoes some important changes, which resemble rather closely similar changes that can be effected in analogous compounds of carbon with nitrogen. Thus it first affords a *guanidine*

$$Si \begin{cases} NHPh \\ =NPh \\ NHPh \end{cases}$$
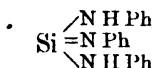
analogous to the well-known carbon guanidine, and further a diimide, $Si (N Ph)_2$, which only needs the addition of a molecule of water to convert it into a silicon *urea*, $SiO (NH Ph)_2$. Many other substances have been produced similar to silicophenylamide, and they afford analogous products to these just mentioned ; but these have been fully described elsewhere, and need not be dealt with here.

SILICON IN RELATION TO ORGANISED STRUCTURES.

The general results of these researches are that we now know a considerable number of silicon compounds including nitrogen, which resemble those of carbon with nitrogen both in composition and in the general nature of the changes in which they can take part. Some of these carbon analogues are closely related to those which are concerned in building up organised structures of plants and animals.

All theories of life assume that its phenomena are inseparably associated with certain complex combinations of the elements carbon, nitrogen, hydrogen and oxygen, with the occasional aid of sulphur and phosphorus. These are the elements of that protoplasm which is the physical basis of life, and by their interplay they form the unstable and complicated groupings of which that remarkable material is composed. All the phenomena we call vital are associated with the change of some protoplasm, and the oxidation of carbon and hydrogen. But it is quite open to question whether the connection of life with the elements first specified is inevitable. We can conceive the existence of similar groupings of other analogous elements forming other protoplasms capable of existing within much greater ranges of temperature than any plants or animals now known to us have to withstand. For example, we can imagine a high temperature protoplasm in which silicon takes the place of carbon, sulphur of oxygen and phosphorus of nitrogen, either wholly or in part. In fact, protoplasm so far as we know it in purest form, always contains some sulphur, and often a little phosphorus, representing a very partial substitution of the kind in question.

In view of our newer knowledge there is therefore nothing very far-fetched in supposing that under suitable conditions a plant or an animal organism, may be able to construct from silicon compounds, ultimately derived from the soil, something akin to silicon protoplasm for use in its structures.

You will now ask me whether there is any evidence that anything of this kind actually occurs in Nature. I think there is, although I admit that the evidence is not very varied as far as we know.

First as to the *Vegetable* kingdom. It is well known that many plants take up silicon in some form from the soil, and use it in ways which my botanical friends tell me they do not at present understand. Silicon is present in the straw of cereals, such as wheat, oats, etc., and in most of the *Gramineæ*. It was supposed that the stiffness of the straw was secured by a siliceous varnish, but this view is not now in favour, as it has been found possible to remove silica from the straw by careful treatment, without diminishing its rigidity. It is also present in the leaves of some palms, for my friend, Dr. Hugo Muller, in the course of his extensive researches on the sugars present in certain palm leaves, has been much troubled by the presence in the extract from the leaves of siliceous compounds of unknown nature. Again, a well-known substance called "Tabasheer," consisting largely of hydrated silica including some organic matter, is obtained at the nodes of some bamboos. What purpose silicon serves in these plants which seem to have special need for it we do not know, but the subject appears to be well worth closer examination than it has yet received at the hands of plant physiologists.

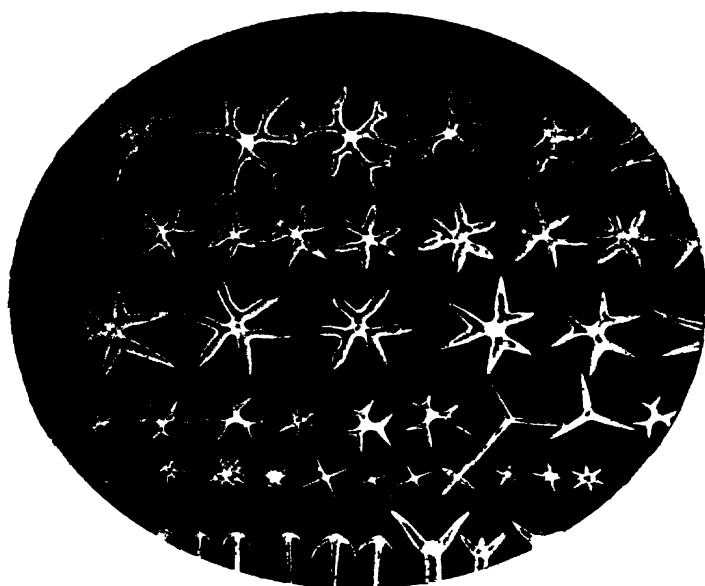I have on the table some good specimens of Tabasheer, and can

Fig 1

Fig 2

show some portions on the screen which have been rendered nearly transparent by soaking in benzene, and under these conditions exhibit traces of structure.

Next as to the *Animal* kingdom. The most satisfactory evidence that we can at present offer as to the organ-building capacity of silicon comes, curiously enough, from some of the simpler organisms of the Animal kingdom, but the only group the short remaining time at my disposal permits me to notice is that of the *Sponges*.

You know that these curious forms of undoubted animal life live in sea-water and are usually anchored to rocks. The sea contains a very minute proportion of silica in solution, and the sponge has the power of appropriating very considerable quantities in the course of its life, and as a part of its normal food supply. What does it do with this silica ? It appears to use it in cell production, and from the cell evolves the beautiful and minute siliceous spicules which are so abundant throughout the structure of many of the sponges.

I have here some photographs of these spicules which I have had taken, and shall throw them on the screen. Two of the best of them have been made from microscopic specimens kindly lent to me by Professor Dendy, of King's College, London, who has made a special study of these spicules and of their modes of growth. One of these slides is reproduced in the engraving. (See Fig. 1 on Plate.)

These structures do not represent mere incrustations, but rather definite growths from the cell protoplasm and are themselves in the nature of cells of characteristic forms. Professor Dendy informs me that these spicules in certain cases become surrounded by a horny substance and seem to die, as if by cutting off the supply of energy as well as growing material.

In some of the larger sponges, as in the beautiful *Euplectella aspergillum* or " Venus' Flower Basket," represented in Fig. 2, the siliceous material constitutes the greater part of the sponge, as the soft portion resembles a somewhat gelatinous coating from which the exquisite siliceous structure is developed.

To sum up, then, I have shown that silicon can easily take the place of carbon in many nitrogen compounds, as well as in others not including nitrogen. It therefore seems to me that we hazard no very violent hypothesis in supposing that the silicon which enters the sponge in its food, probably as an alkaline silicate, is in the marvellous animal laboratory made to take the place of a portion of the carbon of the protoplasm from which the spicules are ultimately developed.

The hypothesis is at any rate suggestive, and I hope enough has been said to commend it to your consideration, for there seems to be · no doubt that silicon is capable of playing a larger part as an " Organic Element," than we hitherto had reason to suppose.

[J. E. R.]

Friday, June 11, 1909.

His Grace The Duke of Northumberland, K.G. P.C. D.C.L.
LL.D. F.R.S., President, in the Chair.

Professor Sir James Dewar, M.A. LL.D. D.Sc. F.R.S. *M.R.I.*,
Fullerian Professor of Chemistry, Royal Institution.

Problems of Helium and Radium.

[Abstract.]

Metallic Vacuum Flasks and Syphons.

Progress in low temperature investigation is greatly aided by careful
attention to questions of method. This observation is specially
applicable to vacuum-jacketed arrangements for heat isolation.
Silvered glass vessels are most useful, and give high isolation, but
are subject to deterioration and collapse, all the more when their
form is complicated. Thus the question of the production of good
metallic vacuum-jacketed apparatus becomes highly important. If
influx of heat by radiation and gas convection is diminished as
much as possible, metallic vacuum-jacketed vessels give no out-
ward sign of the low temperature of their contents. I have here a
lead pipe nearly 100 ft. long (Fig. 1). Liquid air is flowing from
the glass vessel A to the lower one B, which is connected to a
suction pump at C. The pipe shows no sign of frosting or con-
densation of moisture, except at the two ends which dip into the
liquid air. The outside tube is the jacket to a smaller inner tube
(which is externally covered with a layer of flannel) in which the
liquid air is flowing, the annular space between the two tubes being
well exhausted. The vacuum is maintained high by some charcoal
placed in a small enlargement D at the end of the tube dipping
into the liquid air reservoir A.

I have here a double jacketed vacuum vessel of 3 litres capacity,
made of nickel, full of liquid air. A little charcoal placed—as des-
cribed in my Friday Evening Address of 1906 —in the lower part of
the flask, where it is cooled to the temperature of the liquid air, keeps
the vacuum between the walls up to the necessary perfection by
absorbing adventitious gases. The neck of the flask is made of
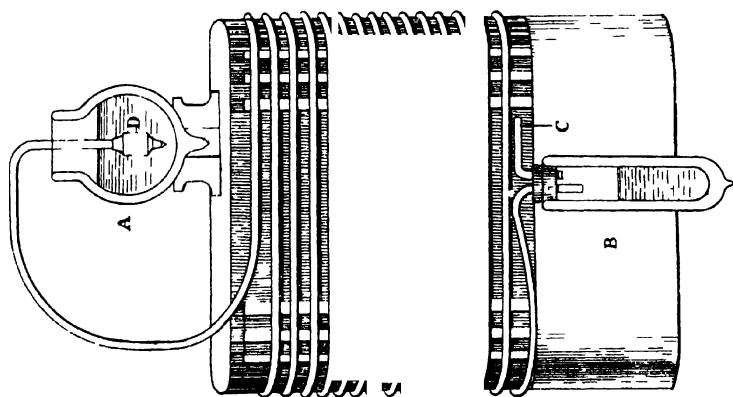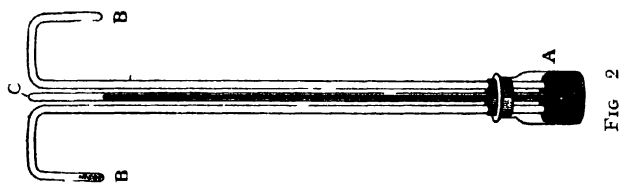thin German silver, a badly conducting alloy, and is covered with a

Fig 2.

Fig. 1.

spiral of worsted cord. This enables a silvered glass vacuum vessel to fit tightly over it and form a kind of open regenerator covering, through which the cold air coming from the evaporating liquid is directed spirally round the neck of the flask, thereby greatly retarding the heat conduction into the inner vessel, which chiefly arises from the outer metallic tube.

COMPARATIVE CONDENSABILITY OF GASES BY CHARCOAL AT LIQUID AIR AND LIQUID HYDROGEN TEMPERATURES.

The relative condensability by charcoal of the gases, air, hydrogen, and helium, can be shown by filling three similar sets of double tubes, shown in Fig. 2, respectively with samples of these gases. The two tubes of each set are filled with the particular gas at atmospheric pressure and the ordinary temperature, and dip into a little bottle of mercury, A. The tubes are bent twice at right angles and sealed up, as shown in the figure. Thus the closed end of either tube of each set can be cooled by immersion in a vacuum vessel containing liquid air or hydrogen. A gramme of charcoal is placed in the sealed end of one tube in each pair. For convenience of pressure observations, an ordinary barometric tube C accompanies each pair of tubes. When the closed end of the air tube is cooled in liquid air, only a small contraction is observed, as shown by a slight rise of the mercury in the tube. If, however, the air tube which contains the charcoal is cooled all the air is thereby condensed, and the mercury quickly rises to the barometer height in the tube. Now take the pair of hydrogen tubes. As before, on cooling the tube without charcoal, only a slight contraction is shown, due to the cooling, but when the charcoal tube is immersed in the liquid air, a quantity of the hydrogen is condensed in the charcoal, and the mercury rises in the tube. The height it attains, however, is noticeably less than in the air-charcoal tube, showing the smaller condensability of hydrogen in the charcoal at liquid air temperature. On cooling either of the helium tubes with liquid air, practically no condensation is shown. Now instead of liquid air, let us use liquid hydrogen, and cool first the air tube. Immediately the mercury rushes up to the barometric height, all the air being condensed into a solid of inappreciable tension of vapour, and the charcoal tube behaves in the same way. Now pass to the hydrogen tubes. When the plain gas tube is cooled, quite a noticeable contraction is visible, because the temperature of liquid hydrogen is so low compared to the hydrogen gas inside at the room temperature. On now cooling the charcoal-hydrogen tube, complete absorption is produced, and the mercury rises to the barometric height. The hydrogen, at the temperature of its own boiling point, is completely absorbed in the charcoal. Now compare this with the set containing helium. On cooling the helium tube it behaves similarly to the plain hydrogen tube, but on cooling the charcoal tube, quite a

large diminution of pressure is produced, showing that even helium is condensed to a considerable extent by charcoal at 20° absolute. As the charcoals warm up, the condensed gases are again expelled ; the helium very rapidly, the hydrogen somewhat more slowly, and the air after some few minutes.

[Brief explanation of low temperature researches with helium, illustrated by slides of the Royal Institution and Onnes Helium Plants ; Reference Diagrams.]

COMPOSITION OF BATH GAS.

	Hydrogen	Nitrogen	Inert Gas
Liquid Bath Gas (most volatile part)	15	30	55

	Helium	Neon
Inert Gas (Bath)	88	17
,, (Air)	16	84

VAPOUR PRESSURES OF LIQUID GASES.

	A	B
1. Oxygen	log. P $= 7\cdot012 -$	$378\cdot3/T$
2. Hydrogen	,, $= 5\cdot981 -$	$63\cdot6/T$
3. Gas same volatility as 1 to 2 ..	,, $= 5\cdot182 -$	$10/T$
4. Helium deduced from charcoal tensions	,, $= 5\cdot324 -$	$11/T$
5 Helium (Onnes)	,, $= 6\cdot496 -$	$16\cdot3/T$

Critical constants and boiling points used in calculating 1, 2, 3, 5.

T is the Absolute Temperature, and P is Pressure in mm. of Mercury.

The B constant is proportional to the Molecular Latent Heat.

——— ‑ ‑

The boiling point of hydrogen is about 20° abs., its critical temperature 32° abs., and the critical pressure 13 atm. The corresponding figures for helium are approximately : boiling point $4\frac{1}{2}°$, critical temperature $5\frac{1}{2}°$, critical pressure about 3 atm. Onnes has, by evaporating liquid helium under reduced pressure, reached a temperature of 3° abs. With the aid of some hypothetical element related in volatility to helium, as helium is to hydrogen, we should be able to reach 1° or possibly even $\frac{1}{2}°$ abs., but not the absolute zero. The experimental approach to the absolute zero has practically been made during the last thirty years. Far greater advances have been made during this period than in the previous 300 years, yet all the new knowledge acquired only shows the need for further research.

Phosphorescence of Gases.—Twenty years ago, I endeavoured in a Friday Evening Discourse to demonstrate the phosphorescence of ozone and oxygen compounds. The effect of the impurities in the air was not then fully recognized. Geissler was the first to discover that phosphorescence may be produced in vacuum tubes. Becquerel considered that oxygen was essential to the production of such phenomena. The new apparatus may be understood by referring to Fig. 3. On the brass cover, A, ground to fit air-tight to a glass
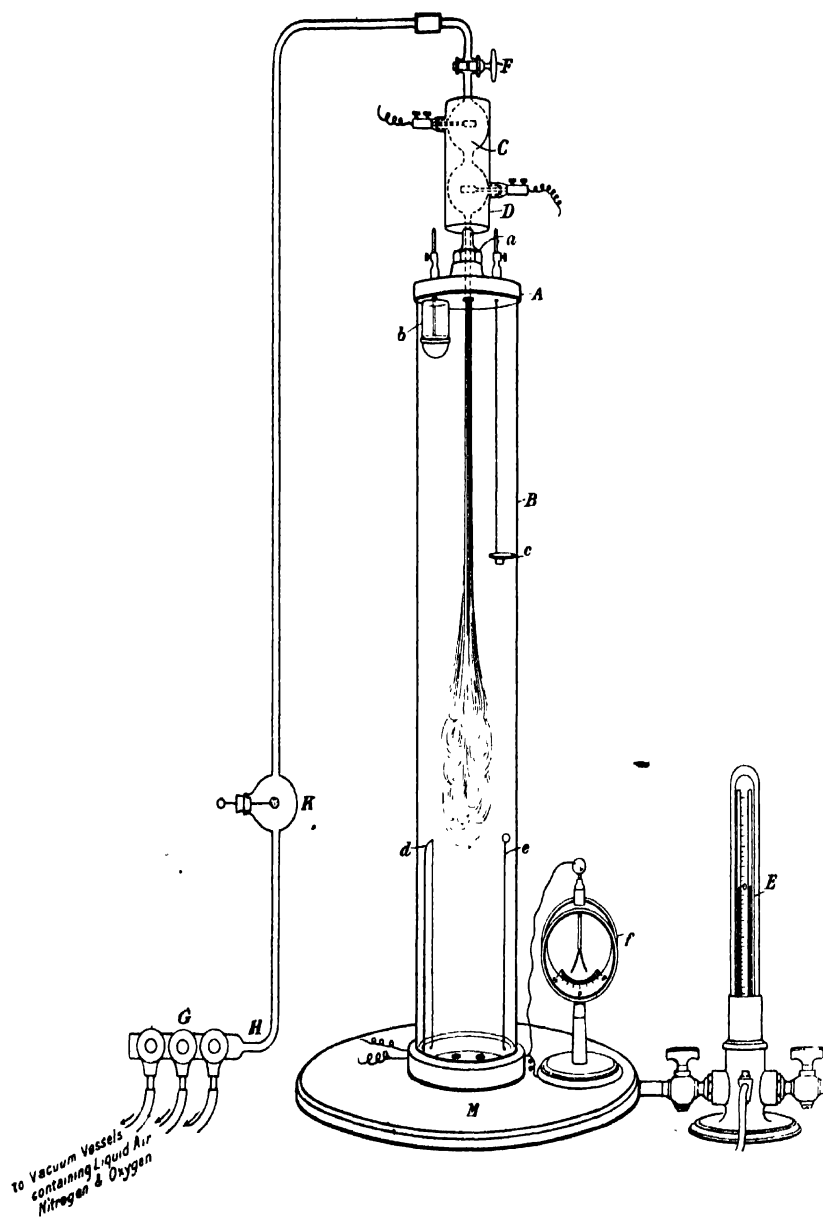
FIG. 3.

cylinder, B, more than 3 ft. in height and 8 in. diameter, is mounted an electric discharge-tube, C, stimulated from a transformer and provided with steel, platinum, aluminium, or other electrodes, about 1 cm. diameter and 4 cm. long, the whole discharge tube being surrounded by a water-jacket, D. An exhaust-pump, capable of dealing with a large leak of gas, while still maintaining a pressure of from 1 to 5 mm. of mercury, is connected to the metal base, M, on which the cylinder is mounted vacuum tight. This base is fitted with stopcocks, and connected to a mercury manometer, E, for controlling the exhaust. The gases are admitted at the top, where they can be regulated by the cock, F.

For obtaining pure air, oxygen and nitrogen, these gases were vaporized directly as required from the respective liquefied gases through narrow lead pipes soldered to the top of brass tubes about 1 ft. long and 1 in. wide, covered over the ends with flannel to act as a filter when dipped into the respective liquids contained in vacuum vessels. The narrow lead pipes are connected to the inlet screw-down regulating valves, G, fixed to the table on which the apparatus is set up, the common outlet tube, H, being connected by another narrow lead pipe to the stop-cock F at the top of the glass cylinder, passing through a small tubulated spherical bulb, K, into which organic and other vapours are introduced by saturating a little cotton wool rolled on the end of a wire with the respective organic liquids. This combination affords a very effective and ready means of obtaining large currents of gas in a state of purity, necessary to ensure good phosphorescence in large scale experiments required for lecture demonstration.

The gas stream is thus seen to form a phosphorescent axial core. The discharge-tube is mounted on a ball and socket union, a, so that the gas stream can be deflected in the cylinder. A glass cup, b, mounted immediately under the top plate of the cylinder, can be turned under the orifice of the discharge-tube so that the entering gas stream impinges into it. The gas stream is thus broken up into a luminous cloud overflowing the cup and filling the upper part of the glass cylinder. A horizontal metal plate, c, can similarly be moved into the stream; this causes a general scattering of the beam. When the air current is started, it rushes down the tube at a velocity of about 1000 ft. a second, and a steady brilliant phosphorescent stream appears down the whole length of the cylinder. On increasing the amount of the entering air, the stream is shortened and assumes a brush-shaped formation. A thermo-junction, d, connected to a reflecting galvanometer, indicates change of temperature when the phosphorescent stream passes over it. Similarly the beam can be deflected on to a small insulated metal sphere, e, connected to a charged electrometer, f. When this is done, rapid discharge of the electrometer shows the ionization of the gas particle forming the phosphorescent stream; even should phosphorescence be

feeble or absent, as with some gases, the ionization can be demonstrated. A long thin glass tube sealed at the end can be inserted through a hole in the top plate of the cylinder and filled with liquid air when necessary. Nitrous acid and nitric peroxide are condensed upon it when placed in the phosphorescent stream. This is proved by the well-known Starch Iodide of Potassium and Griess Reactions. It is extremely difficult when using this large apparatus to prevent the formation of some nitrous acid even if liquid oxygen is evaporated; and thus the proof that the phosphorescence is really due to ozone alone and not to nitrous compounds is not perfectly conclusive. If a current of carbon dioxide is substituted for air, the phosphorescence is marked but much more feeble. Hydrogen gas alone gives no luminosity, and if a trace of hydrogen is added to the phosphorescent stream obtained by the evaporation of liquid oxygen or liquid air the phosphorescence at once disappears. Thus 5 per cent. of hydrogen by volume stops the glow in very pure oxygen, while 10 per cent. is required to arrest the light-stream in air. The rate at which the gas passes through the discharge-tube makes a difference in the intensity of the glow, but the presence of more or less moisture has little effect. A little ether vapour or benzol behaves like hydrogen, arresting all phosphorescence, and the luminosity does not reappear until all the vapour has been carried away by the continually renewed pure gas stream. All volatile organic bodies containing hydrogen stop or diminish the phosphorescence. On the other hand, volatile organic substances containing no hydrogen, such as carbon bisulphide, still give phosphorescence, but pure cyanogen or tetrachloride of carbon vapour give no luminosity. Pure carbon bisulphide and sulphur dioxide vapour alone give good phosphorescent streams—at suitable tensions. The glow with very pure oxygen is short but distinctly more brilliant than that given by air. Nitrogen obtained from the liquefied gas gives only a feeble and very diffuse glow. This gas contains a few per cent. of dissolved oxygen, the presence of which causes the glow, as pure nitrogen gives no visible luminosity with this kind of electric discharge.

RADIUM AND ITS EMANATION.

What has all this to do with Radium? It is now known that bodies like ozone and nitric-oxide are produced from dissociated molecules at very high temperatures under considerable absorption of heat, and that such bodies are unstable. That may give us a clue to the formation of radio-active bodies. In my Friday Evening Address for the year 1888, I remarked: "Ozone is formed by the action of a high temperature owing to the dissociation of the oxygen molecules and their partial recombination into the more complex molecules of ozone. We may conceive it not improbable that some of the elementary bodies might be formed somewhat like the ozone,

but at very high temperatures, by the collocation of certain dis-
sociated constituents and with the simultaneous absorption of heat."
This suggestion of endothermic elements was made fifteen years
before the isolation of radium, and the proof of its continual thermal
emission by the Curies. Rutherford has shown that the de-electrified
particle of the a-rays of radium turns into ordinary helium, and
radium itself has been traced to uranium as its parent. As far as
our knowledge of the emanations of radio-active bodies goes, it would
seem that they are substances a little more volatile than carbon dioxide.
The annexed tables show the relative atomic weights and volatilities
of the Series of Rare gases.

New Constituents of the Atmosphere.

	Atomic Weight	Boiling Point abs.
Helium	4 ..	4°
Neon (new)	20 ..	32
Argon (inactive)	40 ..	87
Crypton (hidden)	82 ..	121
Xenon (stranger)	128 ..	164
x_1	172 ..	
x_2 Radium emanation	222 ..	211

Radium Emanation
Vapour Pressure.

$$\text{A.} \qquad \text{B.}$$

$$\text{Log P.} \quad = 7\cdot626 \quad - \quad 1020/T \left(\begin{matrix} -\ 78° \\ -101° \end{matrix}\right) \text{Rutherford}$$

$$\text{,,} \quad = 7\cdot332 \quad - \quad 941/T \left(\begin{matrix} -55°8 \\ -60°6 \end{matrix}\right) \text{Ramsay}$$

$$\text{,,} \quad = 6\cdot950 \quad - \quad 859/T \left(\begin{matrix} \text{critical} \\ \text{boiling point} \end{matrix}\right) \text{Ramsay}$$

$$\left(\frac{\text{Log P.}}{\text{Xenon}}\right) = 6\cdot963 \quad - \quad 669/T \qquad \text{,,} \qquad \text{,,}$$

The volatilites of the rare gases and that of the emanation of
radium are here expressed by the well-known Rankin equation—

$$\text{Log P} = A - \frac{B}{T}$$

where P and T are the pressure in mm. of Hg and the absolute tem-
perature respectively, and A and B are constants; B is here propor-
tional to the molecular latent heat. The tables thus show that not
only does the emanation fit into a series with the rare gases when
classified chemically, but that also in its chief physical properties it
allows of such a grouping. It seems probable, therefore, that x_1 and x_2,
of which the latter is the radium emanation, together with that from
thorium and actinium, would suitably find a place in this series of
gases. It may be added that the B constant for liquid carbonic
acid is 869; that for sulphuretted hydrogen ᷓ a little lower. The
radium emanation, therefore, is of the same order of volatility as
these substances.

Rate of Formation of Helium from Radium.

I determined the rate of production of helium from radium in an apparatus consisting of a McLeod gauge, in the construction of which no indiarubber joints were used, the mercury reservoir being connected to an exhaust pump, while the elevation and lowering of the mercury was carried out by admitting and exhausting air in the reservoir. The air coming in contact with the mercury, was purified by passage over stick-potash and phosphoric anhydride. Sealed on to the gauge was a long U tube containing ¼ grm. of cocoanut charcoal placed in a small enlargement at the bend, the whole being arranged for liquid air or other cooling for any desired length of time. The object of this cooled charcoal is to take up and condense all adventitious gases, other than hydrogen or helium, which might arise from minute leakage, or otherwise be generated in the apparatus. The radium chloride was contained in a small bottle standing in a cylindrical glass bulb, connected by a T joint to the U tube. To the other arm of the T was sealed a bulb containing about 15 grm. of cocoanut charcoal for producing a high exhaustion in the apparatus when cooled to − 190° C. Fig. 5 shows the arrangement of the apparatus, except that the special joint B there shown was employed subsequently, as described below. The whole apparatus was well exhausted by mechanical means, all the glass tubes being heated as well as the charcoal receptacles and the radium chloride. On immersing the receptacle containing the 15 grm. charcoal in liquid air for some hours, while the ¼ grm. charcoal and the radium chloride were kept hot, an exhaust of 0·00015 mm. was obtained. This charcoal receptacle was now sealed off, and the small ¼ grm. charcoal tube cooled in liquid air. In two hours an exhaust of 0·000054 mm. was reached.

The volume of the gauge and apparatus being approximately 200 c.c., the pressure in the apparatus, gives by a simple calculation the actual volume of gas produced measured at atmospheric pressure and the temperature of the laboratory, and thus the rate of production of helium is obtained. This, referred to the weight of radium present, gives the increment in terms of cubic millimetres of gas per gramme of radium per day. During the first three days the growth of pressure was very small, corresponding to about 0·3 c.mm. per grm. of radium per day. The cooling of the small charcoal was, however, interrupted owing to the holidays. The emanation consequently was not now completely condensed, but diffused into the McLeod gauge, where it had the opportunity of coming in contact with large surfaces of glass which no doubt held traces of organic matter and water. The result would be that hydrogen would be produced, and errors in the determination would accrue. This was practically confirmed in that the growth of pressure observed was very irregular, and a further experiment was carried

out to which these objections did not apply. In this experiment the gauge as well as the connecting tubes were well cleaned out with nitric acid, and all thoroughly dried. The radium, after the 1100 hours in which it was under high exhaustion with frequent heating, was certainly in a more satisfactory condition. Further, to prevent the unchecked action of the emanation throughout the apparatus, the little charcoal condenser was maintained at a degree or two below that of the boiling point of oxygen by the use of old liquid air for a period of about six weeks. A larger quantity of charcoal was used, viz., 1 grm., the more effectively to condense out extraneous gases while leaving any helium substantially unaffected. This charcoal had been treated with chlorine at a red heat, and subsequently with hydrogen.

Beyond this the conduct of the experiment followed the lines of the former one. The mercury pump exhaust was continued for several hours—the charcoal being well heated meanwhile —and was carried to $0 \cdot 002$ mm. The large charcoal bulb was then cooled for several hours in liquid air while continuing the heating of the 1 grm. of charcoal and the radium salt. A pressure as low as $0 \cdot 00005$ mm. was thus obtained when the charcoal was sealed off. On now placing the U tube containing the 1 grm. of charcoal in liquid air the pressure registered was $0 \cdot 000044$ mm.

These conditions were maintained for five days, during which a steady growth of pressure was observed corresponding to an increment of approximately $0 \cdot 3$ c.mm. per grm. of radium per day. The radium was then heated with a small Bunsen flame as before to below a red heat, when the pressure was increased by about 40 per cent. This increase showed no sign of disappearing, but during the next week a decided but somewhat irregular growth of pressure was recorded. The radium was again heated, when a further increase of pressure was observed. In the succeeding five days it remained steady, only to be again increased on heating the radium. This treatment was repeated in all ten times at varying intervals during 1100 hours, and in each case the pressure rose on heating and remained fairly steady on standing. All the observations of the second set of experiments are graphically represented in Fig. 4. A mean line is drawn through the observations taken with the radium heated, giving a steadily maintained helium increment of approximately $0 \cdot 37$ c.mm. per grm. of radium per day.

In order to ascertain if any helium was occluded in the cooled charcoal and the surrounding glass, the latter was raised to near a low red heat while the tube containing the radium chloride was temporarily cooled in liquid air, with the object of condensing out and localising the emanation coming from the heated charcoal and preventing its access to the gauge. The temperature was maintained for an hour, and the charcoal was then allowed to cool, and finally replaced in the liquid air. The radium chloride was then allowed to warm up, and

Increase of pressure in a Mc Leod Gauge with 70 mg Radium Chloride & 1 gm cocoanut charcoal cooled in Liquid Air
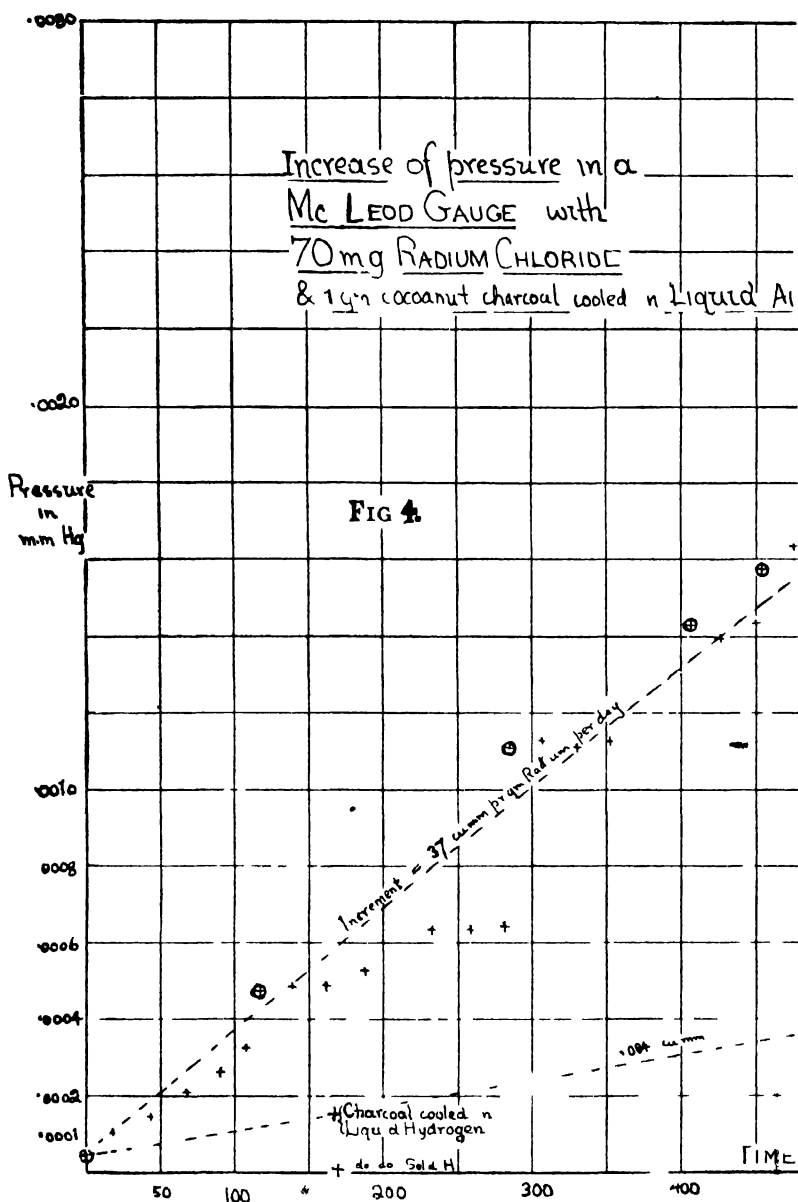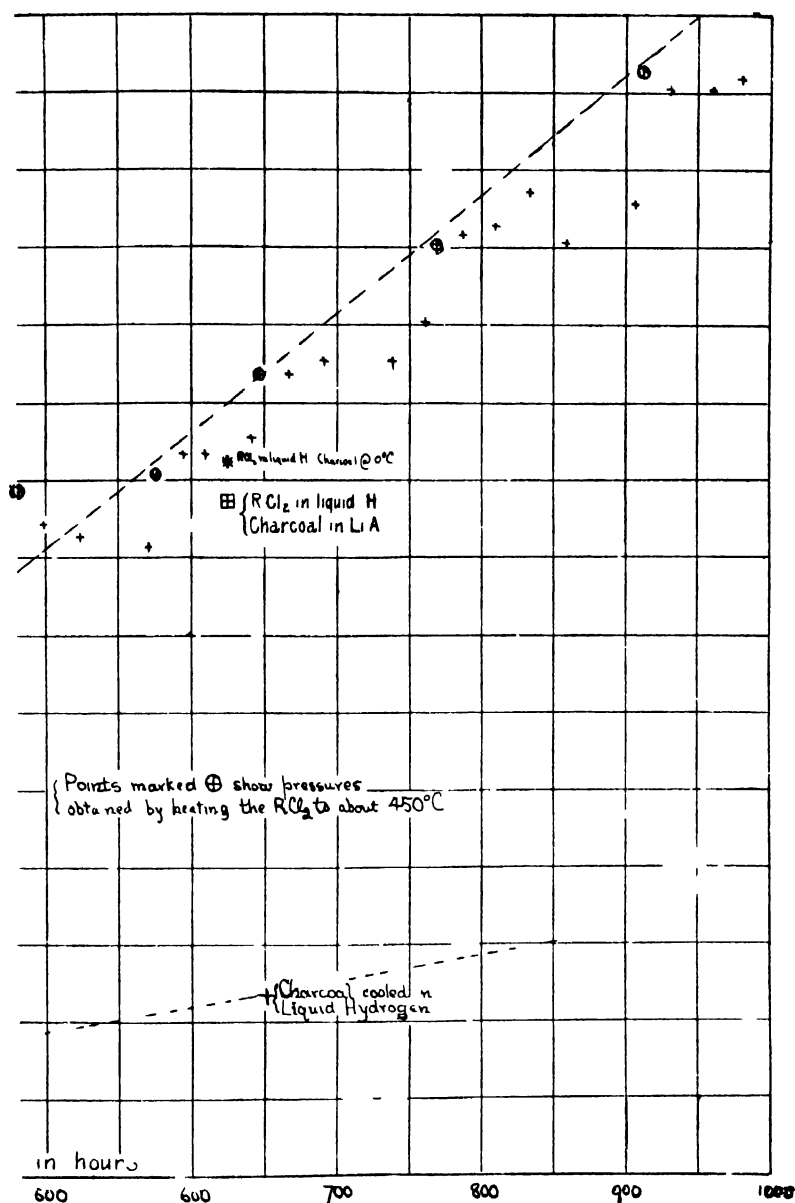
Fig 4.

Fig 4.

was heated to near a low red heat for a short time.   After these alterations no increase in pressure was observed, from which it may be inferred that the occlusion of the helium takes place mainly in that part of the apparatus where the radium chloride is situated.

On two occasions the charcoal was cooled in liquid hydrogen, viz., after 165 hours, and again after 650 hours.   The proportionate reduction of pressure was the same in both cases, tending to show that the composition or nature of the gas remaining uncondensed by the charcoal in liquid air remained the same throughout, although steadily increasing in quantity.

In reference to this last point a separate experiment was made in which pure helium produced by heating $0 \cdot 5$ grm. uranite and passing the gas produced over 1 grm. charcoal cooled in liquid air, was subjected, at a small tension measured on a McCleod gauge, to the action of $\frac{1}{4}$ grm. of clean exhausted charcoal at the temperatures of liquid air and liquid hydrogen respectively.   The ratio of the two pressures so obtained was in close agreement with that observed in the radium experiment.

A further test of the purity of the gas producing the permanent pressure observed in the radium experiment with the charcoal cooled in liquid air was made by simply cooling the bulb containing the radium in liquid hydrogen, allowing the charcoal meanwhile to warm up to 0° C.   If any hydrogen had been present in the gas it is certain that there would have been an increase of pressure recorded, since although hydrogen is partially absorbed by charcoal in liquid air, yet it would not be materially reduced in pressure by cooling in liquid hydrogen.   On allowing the charcoal therefore to warm up, any hydrogen thus expelled would remain and cause an increased pressure.   Inasmuch as an increase was not recorded, it can be safely assumed that no hydrogen was present, and thus the gas pressure measured consisted entirely of helium.

A confirmation of this was obtained spectroscopically as follows : Two tin foil electrodes were placed round the narrow capillary measuring-tube of the gauge, near the closed end.   These were about 3 cm. long and about $1\frac{1}{2}$ cm. apart, and were wired on with thin copper wire.   The gas was compressed into this capillary space, as in taking an ordinary measure, to any pressure of the order of 2 or 3 mm., while an induction discharge passed in the gas.   The spectroscopic examination of this discharge revealed only the six principal helium lines, mercury, and a trace of the carbonic oxide spectrum.   I have shown that the carbonic oxide spectrum always occurs in electrode-less tubes.[*]

The curve showing the rate of production of helium is clearly linear within experimental errors, as shown in Fig. 4.   The volume of the gauge given was unfortunately erroneously estimated, and the
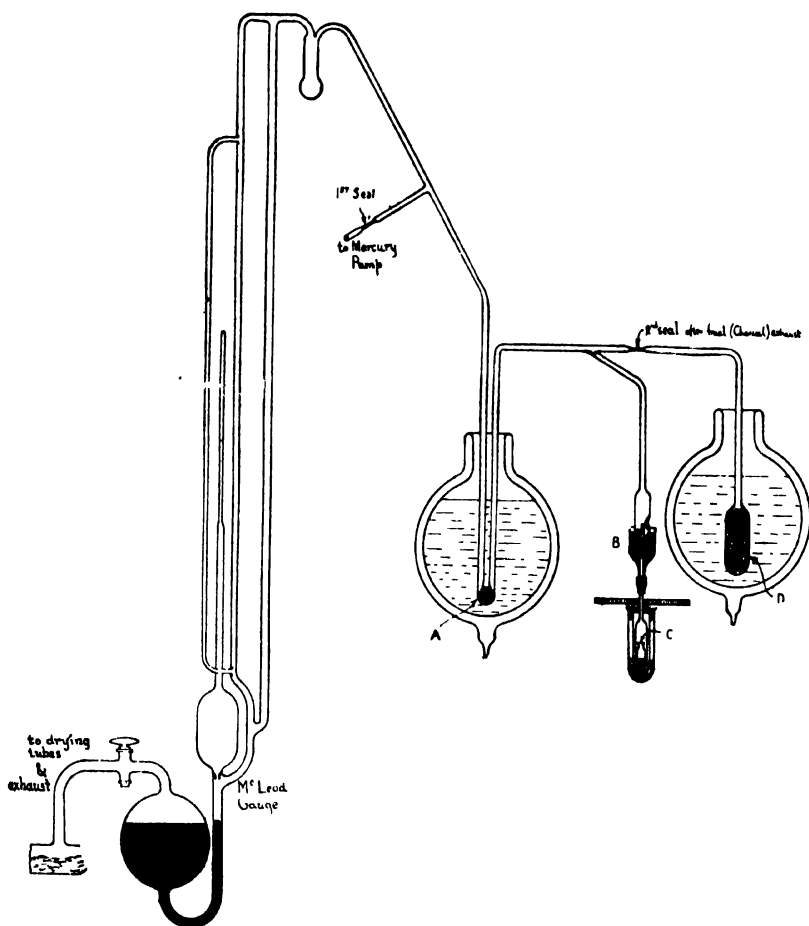
FIG. 5.

correct value was found subsequently to be 270 c.cm. This would give an increment of 0·499 c.mm., which must be taken as the true value obtained from this experiment.

The determination of the rate of production of helium made after a long period of storage was carried out as a confirmatory experiment. Fig. 5 shows the general arrangements of the apparatus used for this determination. A is the 1-grm. charcoal U-tube, D the 15-grm. exhausting charcoal bulb ; the Ra_2 bottle is shown at C. This is similar to that employed in the shorter period determination, with the exception of a special vacuum-tight joint at B. This joint was so constructed that after thoroughly exhausting the gauge, etc., the drawn-out neck of the radium bulb could be broken off, thus allowing the pressure of the accumulated helium from the radium in the bulb to be rapidly determined. Just previous to such breaking the 1-grm. charcoal U-tube was placed in liquid air, in which it remained during all the subsequent operations. The amount of helium produced from 70 m.grm. of radium chloride during nine months was thus measured, and gave a pressure of 0·0163 mm., which is equivalent to a uniform rate of production of 0 463 c.mm. of helium per gramme of radium per day. The experiment was now continued for some five weeks on the lines of the former determinations, observations of pressure being made daily to observe the rate of production of helium from the radium while thus connected with the gauge and cooled charcoal.

At weekly intervals the radium was heated, and a rise of pressure was recorded. Between the times of heating, the pressure fluctuated somewhat, but in general only gave evidence of rising. Through the " heated " observations, which were six in number, the nearest straight line was drawn, as in the earlier experiments. The calculated increment so obtained, however, had a value as high as 1·26 c.mm. of helium per gramme of radium per day. This high value is untenable, and is explained by the action of the radium emanation on the surface of the vaselined rubber joint producing hydrogen, which would remain uncondensed by the cooled charcoal.

Thus we have 0·499 c.mm. as the value of the helium produced from the short-period experiments, and from the long period determinations the value 0·463 is obtained. The actual value is most probably between these two figures.

I am not aware of any previous direct measurements of the rate of production of helium from radium, but in a paper on " Some Properties of Radium Emanation," by A. J. Cameron and Sir William Ramsay,[*] the ratio of the amount of helium produced to that of the emanation was found to be 3·18, and as the amount of the emanation found by them was about 1 c.mm. per gramme of radium per day, the resulting helium, according to this experiment, ought to reach about 3 c.mm.,

* Journ. Chem. Soc., 1907, 1274.

or at least six times the rate of production found in the above experiments. I am at a loss to explain the origin of such grave discrepancies in the measured amount of the helium produced by radium. On the other hand, Professor Rutherford, in his work entitled " Radio-active Transformations," 1906, page 186, on the theoretical assumption that the particle is an atom of helium carrying twice the ionic charge, deduced from electrical measurements that the number of particles expelled per year per gramme of radium would reach 4×10^{18}, and as 1 c.cm. of a gas at standard temperature and pressure contains $3 \cdot 6 \times 10^{19}$ molecules, the volume of helium produced per year would amount to $0 \cdot 11$ c.cm., which is equivalent to about $0 \cdot 3$ c.mm. per day.

It is interesting to note that a more recent calculation made by Rutherford from theoretical considerations of radio-active data, gives a result of $0 \cdot 45$ c.mm. of helium per gramme of radium per day, as compared with the earlier calculation of about $0 \cdot 3$. The agreement between experiment and the theoretical prophecy of Rutherford is remarkable considering the difficulties to be overcome in the observations; substantiating as it does the accuracy of the theory of radio-active changes which he has done so much to develop.

If the helium in the atmosphere was produced chiefly from the radium present in sea-water, Strutt's experiments demand 100 million years for its accumulation. Joly's examination of samples of the ocean beds from the ' Challenger' Expedition revealed the presence of considerable amounts of diffused radium, which would shorten this period. Such conclusions are based on the estimation of very minute quantities of radium, and it is just as likely that 50 million years might suffice to account for all the helium present in the atmosphere as the 100 million year estimate given above.

[J. D.]

Friday, January 21, 1910.

SIR WILLIAM CROOKES, LL.D. D.Sc. For. Sec. Roy. Soc.
Honorary Secretary and Vice-President, in the Chair.

PROFESSOR SIR JAMES DEWAR, LL.D. D.Sc. F.R.S.,
Fullerian Professor of Chemistry.

Light Reactions at Low Temperatures.

[ABSTRACT]

THE physiological action of light was the subject of my first Friday
Evening Lecture. At that time it almost seemed that we should not
materially add to our knowledge of physiological problems by the
application of very low temperatures. Later researches conducted in
conjunction with Professors McKendrick and Macfadyen established
that mere cooling did not destroy putrefying organisms, and also that
other bacilli were not destroyed by continued alternations of warmth
and extreme low temperatures. Seeds which had been kept for six
hours in liquid hydrogen suffered no loss of vitality, neither did
bacteria. It has been thought that chemical action is impossible
at the low temperatures now obtainable, but there are reactions
which are still possible. As an example your attention will be drawn,
among other things, to the results of some recent experiments on
phosphorescent bacteria; these organisms being peculiarly adapted for
investigations of this kind from their special property of producing
luminosity during life.

In dealing with light reactions, care must be taken to exclude the
action of the radiant heat which always accompanies it. This involves
the need of some arrangement like a water cell built up with quartz
windows, which absorbs heat but is transparent to invisible light of
short wave-length.

Experiments showing some effects of light radiation.—Here is a
tall glass jar containing some chlorine peroxide, a yellow gas mixed
with the air. When the radiation from the arc lamp is made to pass
through it, decomposition is at once evident from the clouds which
are formed.

The change of colour by cooling which is shown by some substances
is of a different order. A strip of paper coated with red iodide of
mercury can be cooled by simply dipping half-way into liquid air.
The effect is to change the red to yellow in the cooled region.

The fluorescent appearance of some bodies when exposed to light is
well known. This tall cylinder contains simply water, illuminated by

a vertical beam of violet light reflected in from an arc lamp. A few minute fragments of solid eosin thrown in, gradually dissolve, producing a red solution. The specks of eosin as they fall through the water leave behind a brilliant yellowish fluorescent track which soon permeates the whole solution. The violet rays are absorbed by the eosin, and subsequently emitted in the form of this beautiful greenish yellow colour.

A somewhat similar fluorescent or phosphorescent effect is produced by some bodies at low temperatures. On the outside of this long test tube is spread some ordinary egg albumen. This can be cooled down and frozen by simply pouring a little liquid air into the tube. When exposed to the light of the arc the frozen albumen shows a beautiful blue phosphorescence. A second tube covered with glycerin and similarly frozen shows a like effect. Zymase or yeast juice, obtained by breaking up yeast-cells and extracting the liquid contents, shows marked phosphorescence. All culture media used in bacteriological research behave in the same way. An ivory paper-knife cooled by dipping into liquid air phosphoresces brightly. A strip of gelatin behaves in the same manner, so also an ordinary paraffin candle

These substances all show phosphorescence at the low temperature. Calcium sulphide on the other hand is a body which will phosphoresce at ordinary temperatures, and it becomes interesting to see what will be the effect of cooling on this luminous paint. This star-shaped piece of cardboard, which has been coated with calcium sulphide, shows strong phosphorescence at the ordinary temperature. Now float it on some liquid air in a dish, and you observe the light becomes dim and disappears. Warm it up by merely waving it in the air, and very soon it again gives out its characteristic light. This vacuum vessel contains a similar star which has been kept in liquid air for 24 hours. On taking it out the dark star becomes brightly luminous. Its phosphorescing properties are stored up or rendered latent so long as the low temperature is maintained. In order to become phosphorescent the body must first be exposed to light. It is interesting to see whether cooling to the temperature of liquid air before and during such an exposure has the effect of preventing subsequent phosphorescence. A similar sulphide of calcium cardboard star which has not been exposed to light and is consequently non-luminous at the ordinary temperature, is floated in an aluminium dish on the surface of liquid air, and when thoroughly cooled to − 185°, exposed to violet light. All remains dark, but on allowing it to warm up we see that light-energy must have been absorbed at the low temperature, because the star now phosphoresces in a marked degree. If this experiment is repeated, using liquid hydrogen instead of liquid air, the same effects are observed.

All these substances absorb ultra-violet light and transform it into visible phosphorescence. By a similar absorption other bodies, however, possess the power of yielding other forms of energy. The

case of oxygen is interesting. This is transparent to heat, but has many absorption bands for light in the visible spectrum, and also has the power of absorbing the ultra-violet. Nitrogen, on the other hand, is relatively transparent. An ordinary spectrum is shown on the screen. A flask containing liquid oxygen is introduced into the beam, and several dark bands are produced, showing the absorptive power of the liquid. A similar vessel of liquid nitrogen, however, shows no such bands. These two spherical vacuum flasks of liquid oxygen and liquid nitrogen respectively can be placed in the parallel beam of the arc, and it will be seen that they both act as an ordinary lens and converge the light to a focus. On holding a piece of black paper in the focus, very soon a hole is burnt through and the paper ignites, the heat rays being evidently transmitted. We will now project a few photographs of absorption spectra of both liquid nitrogen and liquid oxygen admixed with it in various proportions, also similar slides of absorption spectra of yeast juice, gelatin, glycerin, etc., etc. These photographs were taken with a quartz spectrograph, using for the most part a cadmium-magnesium spark. All the photographs show marked absorption in the region of the ultra-violet.

Photo-electric Cells. — Cells can be constructed whereby light energy can be transformed into electrical energy. This cell has plates of silver coated with chloride of silver, placed in dilute sulphuric acid in a quartz tube, and is connected to a reflecting galvanometer showing a spot of light on the scale. When light is allowed to fall on one of the plates a deflection takes place. The chemical decomposition produced by light is transformed into electrical energy, causing an electric current. Other forms of light cells filled with liquid mixtures sensitive to light have been used in recent experiments. Their general construction is shown in Plate I. figs. I. and II. A is a fine platinum wire (secured in the paraffined cork in the base of the tube), drawn tight against the inner surface, and fixed over the top edge by soldering on to stouter copper wire wound round the outside of the top of the tube. A thick platinum wire B is placed at the back to act as the second electrode. The cell is conveniently mounted in a paraffin block in which are two depressions for mercury cups to connect the two electrodes. A is thus made to enclose a thin film of liquid between itself and the wall of the tube. Any change in the composition of this external film will not diffuse rapidly into the cell liquid, and thus differences of electrical potential so produced will be detected by means of the galvanometer. One of the two cells on the table contains a saturated aqueous solution of chlorine peroxide, the other a 20 per cent. solution of uranium nitrate in methyl alcohol.

When a beam of light from the lantern is directed on to the chlorine peroxide cell a good deflection of the galvanometer is observed. On shutting off the light the disturbance soon passes away, as a uniform diffusion in the cell is effected. The uranium nitrate

shows an even greater deflection, which does not die away so quickly unless we short circuit the cell. Such electrical effects depend upon the temperature of the cell. On cooling the uranium nitrate cell with a pad of cotton wool saturated with liquid air the alcohol will be cooled down to its freezing point, and now no electrical action takes place. In fact a temperature of only − 80° C. is sufficient to arrest any current, the solution being then congealed to a jelly.

The ordinary photographic action of light is similarly prevented by cooling to a low temperature. A piece of photographic paper kept cooled locally in a patch of about 3 in. diameter by a cotton wool pad soaked in liquid air while exposed to the electric beam is blackened, except in the cooled patch which remains unacted upon.

The photographic action of ordinary light is largely restricted to the ordinary temperature. When we come to ultra-violet light we have a different state of things. This radiation is capable of producing effects at the temperature of liquid air and even liquid hydrogen. A convenient and powerful source of ultra-violet light is the electric arc in mercury vapour contained in silica tubes. Glass tubes would of course absorb the ultra-violet light besides being liable to fracture from the high temperature of the lamp. An arc between copper and carbon poles in air is also available as a source of ultra-violet light, but is not so convenient to work as a modern mercury vapour lamp. In all my later experiments on phosphorescent bacteria the mercury lamp has been used. The general arrangement of the apparatus is shown in Plate II. figs. I. and II. Liquid oxygen is highly absorptive of the ultra-violet light. If a few cubic centimetres of liquid oxygen are poured into a shallow silver dish floating on liquid air, and a quartz cell containing water to the depth of a centimetre is arranged to absorb the bulk of the heat radiation, the ultra-violet rays can continue to act on the liquid oxygen for a considerable time. Pouring the remaining liquid oxygen into an ordinary glass beaker, in which are suspended some strips of paper treated with potassium iodide and starch solution, the presence of ozone in the evaporating liquid is evident from the dark blue colour produced. To prove that this is the effect of the ultra-violet radiation the experiment will be repeated, with a very thin lamina of mica, which is opaque to the ultra-violet, interposed between the mercury lamp and the liquid oxygen. In this case no ozone is produced, the strips of paper remaining quite white after the exposed oxygen is poured into the beaker. The smell of ozone during the evaporation of the liquid air is the most delicate and characteristic property of the body. If the ozone has to be estimated quantitatively, then the liquid oxygen after exposure to the ultra-violet radiation of the arc or mercury lamp is transferred to a small vacuum vessel B (Plate I. fig. IV.) and allowed to slowly evaporate, the gas being bubbled through iodide of potassium solution in the vessel A. In order to prove that the formation of ozone can take place in liquid oxygen, avoiding any action on the gas, a quartz vacuum vessel (Plate I. fig. III.) had a

concentrated beam from the arc condensed in the liquid by means of a quartz lens D. After an hour's exposure ozone could easily be recognized.

The exposure at liquid hydrogen temperatures is somewhat too dangerous to carry out on the lecture table, but solid oxygen in liquid hydrogen contained in a quartz vacuum tube has also been subjected to the ultra-violet radiation. When the liquid hydrogen evaporated away, ozone came off from the liquefied oxygen during its evaporation, so that the production of ozone was still possible even at 20° A. from the impact of ultra-violet rays on solid oxygen.

Experiments on the action of ultra-violet light on phosphorescent bacteria at low temperatures.—The *Photobacterum phosphorescens* is also known as *Photobacterium phosphorescens gelidus*. It is the most widely distributed and best known of all photogenic bacteria. It occurs on the bodies of nearly all dead fish and is most easily obtained from dead herring or mackerel. The light emitted by this Bacillus is of a brilliant green colour which provides an easy means of identification. The culture-medium must contain certain inorganic salts characteristic of sea-water. A good artificial culture-medium has the following composition :—

```
1 litre of beef broth peptone gelatine.
Sodic chloride ..    ..   ..   ..   ..   ..   26·5  grammes.
Potassic chloride  ..   ..   ..   ..   ..    0·75    ,,
Magnesic chloride ..  ·.   ..   ..   ..    3·25    ,,
```

The microscopic appearance of these bacteria at different ages, and also when grown in different culture media, are shown in Plate III. Several cultures of these organisms, kindly prepared by Mr. Henry Crookes, are on the table. At the temperature of the room they are very bright. This large shallow tin vessel contains a good bright culture, and on to it some liquid air can be poured, which rapidly destroys the luminosity of the bacteria. The organisms are not killed, for on waving the tin in the air, thus allowing it to warm up, the brightness again appears. While the organisms are at liquid air temperature they can be exposed to the action of ultra-violet light. For this purpose a smaller culture in a tin dish is floated on liquid air by the arrangement shown in Plate II. fig. 1. A is a tin or aluminium dish about 10 cm. wide and 2 cm. high, in which is placed the smaller dish containing the culture. This arrangement is supported by a cork float on the liquid air contained in a glass silvered hemispherical vacuum vessel B. On B, a shield C rests, consisting simply of two polished sheets of tinned iron, fixed at a small distance apart, which protects the liquid air in B from the heat radiation. C is pierced by a central hole rather wider than A, in which a quartz-dish D, about 1 cm. high, is placed, filled with water to act as a heat filter. This arrangement can be placed either under the arc or the mercury lamp, whichever is being employed.

Five minutes' exposure at a distance of a few inches from the mercury lamp is usually sufficient to kill the bacteria when they are

located on the surface layer of the culture medium. The exposed culture is taken out and allowed to warm up in the air. No brightness supervenes even after the culture is kept for several hours. A few colonies will occasionally develop on keeping for a day, but this is because the growth of the bacteria has extended downwards into the medium, and are thus protected from the radiations, since a thin layer of the culture medium is sufficient to absorb the ultra-violet. If a metal plate, out of which a cross has been cut, or perforated metal is placed on the surface of the frozen bacteria before exposure to light, the appearance of the surface of the bacteria when allowed to heat up to the ordinary temperature is shown in Plate IV. fig. 11.

There are sources of deception possible in this work, unless proper precautions are taken. If the dish containing the culture is floated direct on the liquid air, and especially if it be heavy, causing the level of the culture to be below that of the exterior liquid air, it frequently happens that a thin layer of liquid oxygen makes its appearance on the surface of the culture, either by condensation at the lower level, or by capillary action, or even spraying. In this case we have the complications produced by the absorption of the ultra-violet light by the thin oxygen layer, and the possible action of the ozone produced. In many cases surprising results were obtained, in which the organisms seemed to remain alive even after long exposures. In addition to this there was the possibility of condensation on the cold culture of both moisture and oxides of nitrogen, the latter always present in the air round such a mercury lamp, although while the culture is in the liquid air, the atmosphere over it is for the most part kept clear of contamination by the evaporating oxygen and nitrogen. Another arrangement was used in order to allow the ultra-violet radiation to act on the bacteria in an atmosphere of hydrogen or pure nitrogen, thus eliminating any of the secondary reactions mentioned above. Plate II. fig. 11. shows such an arrangement. A simple thin sheet metal box M is fitted with a quartz cover N, which slides tightly into it. The dish A, containing the culture, is placed in M, into which also a narrow lead pipe P opens. The whole arrangement can be supported by P in any position in the vessel of liquid air. Through P hydrogen or nitrogen can be passed, the excess escaping round the joint of M and N. Adopting such precautions made no difference in the efficiency of the ultra-violet in killing off the bacteria at low temperatures.

The luminosity of these bacteria may remain latent for considerable periods. Oxygen is necessary for their activity, but they will remain alive, although dark, if air be excluded for several weeks, although they then need a little time to develop their activity. The curves of Plate IV. fig. 1. are interesting, and show the rate of growth of two identical colonies in air and a vacuous flask respectively. The ordinates represent the diameter of the colonies in millimetres. The abscissæ show the age in days. Curve No. (11)

shows the growth in a flask kept vacuous for fifteen days, and then opened to the air. Curve (I) is the growth of a colony in an ordinary open flask, which, however, was exhausted and sealed on the fifteenth day. Curve (II) is practically a horizontal line during the fifteen days of exhaustion, showing no development of the colony, whereas during this time curve (I) shows a steady increase. After the fifteen days, however, curve (II) begins to develop, and shows an increase corresponding to the opening of the exhausted flask. The effect of oxygen can be illustrated by a few experiments. This flask contains some broth culture of these bacilli, and is only feebly luminescent, but on bubbling oxygen through the liquid the froth so formed is exceedingly bright, the bacteria being excited by the oxygen to great activity. Here are three flasks over the interior surface of which some phosphorescent culture medium has been spread, followed by exhaustion of the flasks. They have remained so for one, two, and three weeks respectively. Upon opening these flasks the luminescence will once more re-establish itself by the action of the oxygen so admitted, although (especially in the case of the three weeks' old culture) its full brightness will not develop for 24 hours.

The phosphorescent bacteria behave differently towards various metals. Various cultures have been prepared, and plates of various substances placed thereon, and remarkable effects obtained. Some reproductions of these are shown (Plate V. figs. 1 to 6). Thus, a disk of zinc caused death to the organisms in a considerable zone surrounding it. Similarly, also, copper and silver, and especially mercury, which is particularly fatal. Tin, on the other hand, is inactive.

A piece of the metal whose effect it is desired to examine is placed in the centre of the tin dish containing the medium infected with the phosphorescent bacteria. The growth of the phosphorescence is then observed. Several metals have no apparent effect. Among these are gold and the platinum group, tantalum, cadmium, magnesium and tin. Similarly coconut charcoal, graphite, and selenium have no effect. Sulphur seems actually to stimulate the bacteria which cluster brilliantly round it on the culture, leaving the rest of the plate relatively dark. The metals which have been found to slightly check the growth in their neighbourhood are bismuth, thallium, lead and nickel. The alloys German silver, hard brass, and aluminium bronze have also only a slight effect. A stronger action is shown by iron, aluminium, zinc, copper and soft brass. The more deadly metals are cobalt, silver, mercury, antimony, arsenic, and phosphor bronze. Chloride and bromide of silver, cyanide of mercury, and arsenous acid also kill the bacteria. The destructive effect of the metal clearly depends on its slow solution at the ordinary temperature in the saline organic culture medium, aided no doubt by the presence of atmospheric oxygen in some cases.

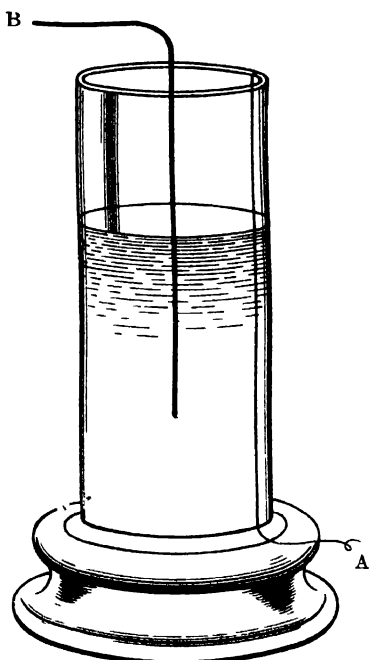The following table gives a list of the metals used and their effects on the bacterium.

PLATE I
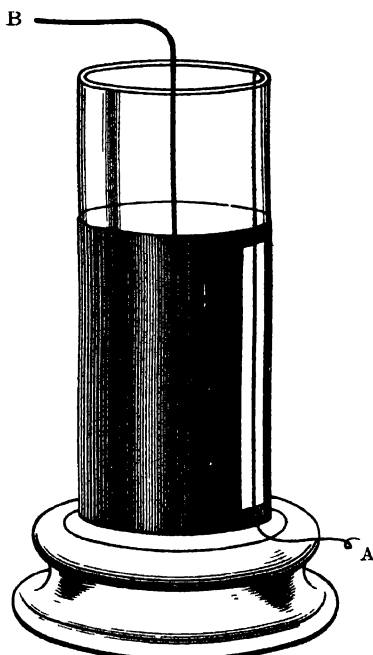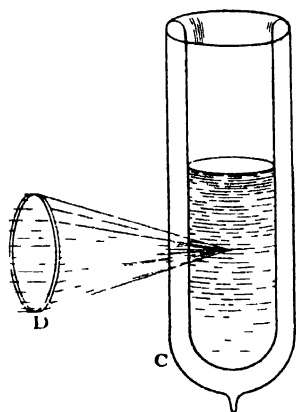
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FIG. I.   FIG II.

FIG. III.   FIG IV.

PLATE II

FIG I

FIG. II.

PLATE III

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89
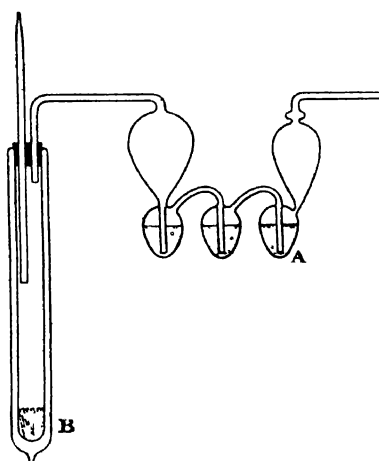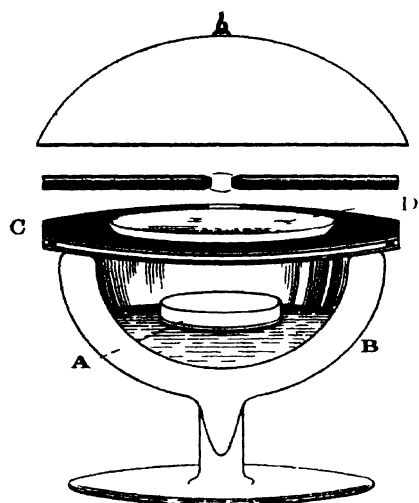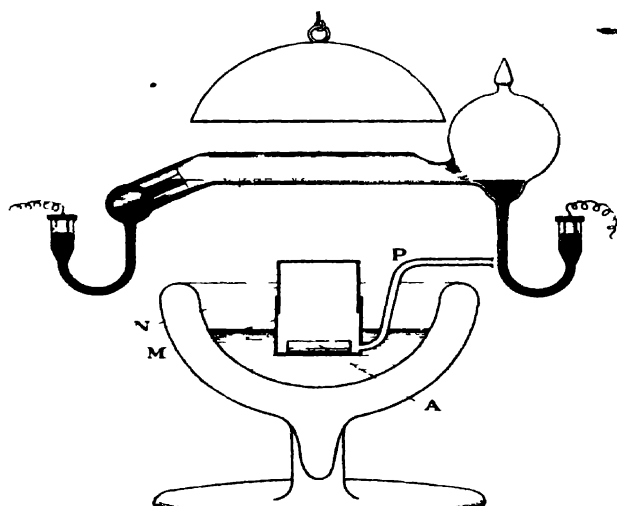
PHOTOGENIC BACTERIA
(*Photobacterium Phosphorescens*)

GROWTH ON SOLID MEDIA	GROWTH IN FLUID MEDIA

GROWTH ON SOLID MEDIA

Fig 1   Fresh culture, ordinary gela-
        tine
,, 2.   Three days' growth
,, 3.   One day's growth, salted
        gelatine.
,, 4.   Old culture, salted gelatine

GROWTH IN FLUID MEDIA

Fig 5   Peptone sea-water
,, 6.   Peptone sea-water, showing
        Flagellum

PLATE IV.

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FIG I —GROWTH OF TWO COLONIES IN DIAMETERS OF B PHOSPHORESCENS
REPRESENTED GRAPHICALLY

(I)   In exhausted sealed tube for 13 days, then opened to the air
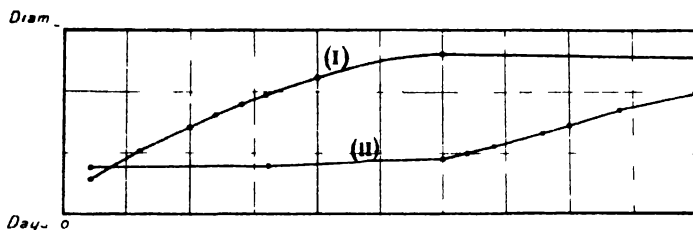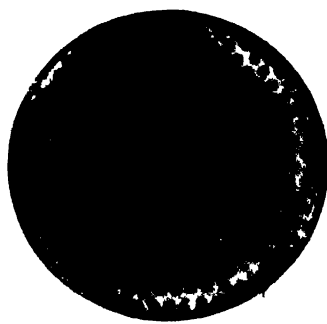(II) In free air for 15 days, then exhausted

FIG II —REPRODUCTION OF PHOTOGRAPHS taken by light emitted by Bacteria
after the action of ultra violet light on them at the temperature of liquid
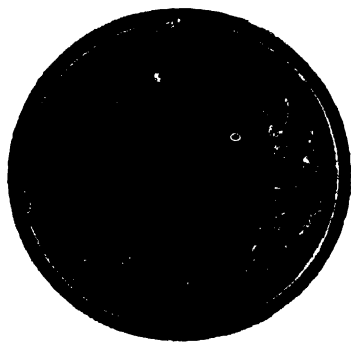air and subsequent heating to the ordinary temperature

1   2

1   Round tin plate with cut out cross, bacteria killed where unscreened
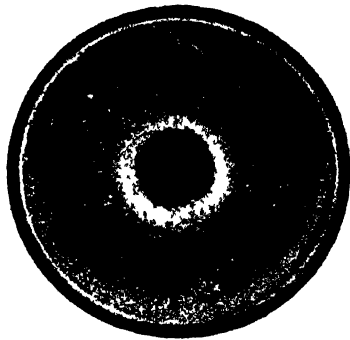2   Perforated zinc, showing same effect as above

PLATE V

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1. Mercury,
2. Antimony.
3. Zinc.
4. Silver.
5. Chloride of Silver.
6. Sulphur.

ACTION OF METALS ON B. PHOSPHORESCENS.

No Action	Partial Action	Strong Action
Gold	Bismuth	Cobalt
Platinum	Thallium	Silver
Palladium	Lead	Mercury
Rhodium	Nickel	Antimony
Iridium	German silver	Arsenic
Tantalum	Hard brass	Phosphor-bronze
Cadmium	Aluminium bronze	
Magnesium		Chloride of silver
Tin		Bromide of silver
Graphite	**Strong Action**	Cyanide of mercury
Cocoanut charcoal		Chloride of mercury
Selenium		(HgCl₂)
Sulphur (stimulates)	Iron	
	Aluminium	Arsenious acid
	Zinc	
	Copper	
	Soft brass	

Other bacteria have been exposed to the action of ultra-violet light. *Bacillus prodigiosus, B. coli communis, B. subtilis,* as well as *B. phosphorescens* are all killed by the action of this radiation at the temperature of − 185° C.

It is remarkable that any radiation effect should take place in these organisms at liquid air temperature, when of course they are hard solids, and no question of ordinary chemical interaction between liquids or gases is possible, as in the case of such powerfully reacting agents as fluorine and liquid hydrogen, which explode violently when brought together under such conditions. Ozone from solid oxygen is, of course, another example of a chemical change taking place at the boiling point of hydrogen, which in this case is induced by the ultra-violet radiation. Any action that takes place must be in the solid contents of the bacteria, which seem to be actually broken up, when examined microscopically after exposure to the ultra-violet light. Perhaps the production of electrically charged ions through the action of the short wave length radiation on the surface of the solid organisms, is a potent factor in their destruction at low temperatures. In any case, it seems the protoplasmic molecule cannot stand the internal strain produced by the vibrations set up in it by the action of the rays of short wave-length, and is thereby forced to re-arrange its atomic structure, causing the death of the organism.

These are only a few indications that there is still much low temperature chemistry to be worked out.

[J. D.]

Friday, February 25, 1910.

SIR WILLIAM CROOKES, LL.D. D.Sc. F.R S., Honorary Secretary
and Vice-President, in the Chair.

THE RIGHT HON. LORD RAYLEIGH, O.M. D.C.L. LL.D. D.Sc.
F.R.S. *M.R.I.*
Honorary Professor of Natural Philosophy, Royal Institution.

Colours of Sea and Sky.

A RECENT voyage round Africa recalled my attention to interesting
problems connected with the colour of the sea. They are not always
easy of solution in consequence of the circumstance that there are
several possible sources of colour whose action would be much in the
same direction. We must bear in mind that the absorption, or
proper, colour of water cannot manifest itself unless the light traverse
a sufficient thickness before reaching the eye. In the ocean the
depth is of course adequate to develop the colour, but if the water is
clear there is often nothing to send the light back to the observer.
Under these circumstances the proper colour cannot be seen. The
much admired dark blue of the deep sea has nothing to do with the
colour of water, but is simply the blue of the sky seen by reflection.
When the heavens are overcast the water looks grey and leaden : and
even when the clouding is partial, the sea appears grey under the
clouds, though elsewhere it may show colour. It is remarkable that
a fact so easy of observation is unknown to many even of those who
have written from a scientific point of view. One circumstance
which may raise doubts is that the blue of the deep sea often looks
purer and fuller than that of the sky. I think the explanation is
that we are apt to make comparison with that part of the sky which
lies near the horizon, whereas the best blue comes from near the
zenith. In fact, when the water is smooth and the angle of observa-
tion such as to reflect the low sky, the apparent blue of the water is
much deteriorated. Under these circumstances a rippling due to
wind greatly enhances the colour by reflecting light from higher up.
Seen from the deck of a steamer, those parts of the waves which
slope towards the observer show the best colour for a like reason.

The real colour of ocean water may often be seen when there are
breakers. Light, perhaps directly from the sun, may then traverse
the crest of the waves and afterwards reach the observer. In my
experience such light shows decidedly green. Again, over the screw

of the ship a good deal of air is entangled and carried down, thus providing the necessary reflection from under the surface. Here also the colour is green.

The only places where I have seen the sea look blue in a manner not explicable by reflection of the sky were Aden and Suez. Although the sky was not absolutely overcast, it seemed that part at any rate of the copious, if not very deep, blue was to be attributed to the water. This requires not only that the proper colour of the water should here be blue, but also the presence of suspended matter capable of returning the light, unless indeed the sea bottom itself could serve the purpose.

The famous grotto at Capri gives an unusually good opportunity of seeing the true colour of the water. Doubtless a great part of the effect is due to the eye being shielded from external glare and so better capable of appreciating the comparatively feeble light which has traversed considerable thicknesses of water. The question was successfully discussed many years ago by Melloni, who remarks that the beauty of the colour varies a good deal with the weather. The light which can penetrate comes from the sky and not directly from the sun. When the day is clear, the blueness of the sky co-operates with the blueness of the water.

That light reflected from the surface of a liquid does not exhibit the absorption colour is exemplified by brown peaty water such as is often met with in Scotland. The sky seen by reflection is as blue as if the water were pure. But an attempt to illustrate this fact by experiment upon quite a small scale was not at first successful. A large white photographic dish containing dark brown oxidized " pyro " was exposed upon the lawn during a fine day. Although the reflected light certainly came from the clear sky, the colour did not appear pronounced, partly in consequence of the glare of the sunshine from the edges of the dish. The substitution of a dish of glass effected an improvement. But it was only when the eye was protected from extraneous light by the hands, or more perfectly by the interposition of a pasteboard tube held close up, that the blue of the reflected light manifested its proper purity. It would seem that the explanation is to be sought in diffusion of light within the lens of the eye, in consequence of which, especially in elderly persons, the whole field is liable to be suffused with any strong light finding access.

As regards the proper colour of pure water, an early opinion is that of Davy, who, in his " Salmonia," pronounces in favour of blue, basing his conclusion upon observations of snow and glacier streams. The latter, indeed, are often turbid, but deposit the ground-up rock which they contain when opportunity offers, as in the lake of Geneva. A like conclusion was later put forward by Bunsen on the basis of laboratory observations. The most elaborate experiments are those of Spring, who, in a series of papers published during many years,

discusses the difficult questions involved. He tried columns of great length—up to 26 metres ; but even when the distance traversed was only 4 or 5 metres, he finds the colour a fine blue only to be compared with the purest sky-blue as seen from a great elevation. But when the tubes contain ordinary water, even ordinary distilled water, the colour is green, or yellow-green, and not blue.

The conversion of the original blue into green is, of course, explicable if there be the slightest contamination with colouring matter of a yellow character—i.e. strongly absorbent of blue light. Spring shows that this is the effect of minute traces—down to one ten-millionth part—of iron in the ferric state, or of humus. The greenness of many natural waters is thus easily understood. Another question examined by Spring is not without bearing upon our present subject—viz. the presence of suspended matter. I am the better able to appreciate the work of Spring, that many years ago I tried a variety of methods, including distillation *in vacuo*, in order to obtain water in the condition which Tyndall described as " optically empty," but I met with no success. Spring has shown that the desired result may be obtained by the formation within the body of the liquid of a gelatinous precipitate of alumina or oxide of iron, by which the fine particles of suspended matter are ultimately carried down.

Perhaps the most telling observations upon the colour of water are those of Count Aufsess, who measured the actual transmission of light belonging to various parts of the spectrum. The principal absorption is in the red and yellow. In the case of the purest water, there was practically no absorption above the line F, and a high degree of transparency in this region was attained even by some natural waters. That these waters should show blue, *when in sufficient thickness*, is a necessary consequence.

In my own experiments, made before I was acquainted with the work of Aufsess, the light traversed two glass tubes of an aggregate length of about 4 metres (12 feet). On occasion the light was reflected back so as to traverse this length twice over. I must confess that I have never seen a blue answering to Spring's description, when the original light was white. For final tests I was always careful to employ the light of a completely overcast day, which was reflected into the tubes by a small mirror. The colour, after transmission, showed itself very sensitive to the character of the original source. The palest clear sky of an English winter's day gave a greatly enhanced blue, while, on the other hand, isolated clouds are usually yellowish, and influence the result in the opposite direction. I should myself describe the best colour of the transmitted light on standard days as a greenish blue, but there is some variation in the use of words, and, perhaps, in vision. Some of my friends, but not the majority, spoke of blue simply, but all were agreed that the blueness of a good sky was not approached. The waters tried have been

very various. Sea-water from outside the grotto of Capri, from Suez, and from near the Seven Stones Lightship off the Cornish coast, I owe to the kindness of friends. Of these the two former showed a greenish blue, the latter a full, or, perhaps, rather yellow-green, and these colours were not appreciably modified after the water had stood in the tubes for weeks. It is important to remember that the hue may, to some extent, depend upon thickness. It is quite probable that in a greatly increased thickness the Capri and Suez waters would assume a more decided blue colour. But I do not think the Seven Stones water could so behave, the colour, with 12 feet, seeming to involve the absorption of blue light.

Further observations on greater depths of sea-water would be desirable. A naval son informs me that off the coast of Greece a plate lying in 6 fathoms of water looked decidedly blue, although the sky was a dirty grey. I have doubts whether this would be generally the case in the Mediterranean; the green due to moderate thicknesses seems too decided.

Of natural fresh waters that I have tried, none were better than that from a spring in my own garden. This water is hard, but bright and clear, and it shows a greenish-blue, barely distinguishable from that of the Capri and Suez water. Distillation does not improve the blue. Neither did other treatments do any good, such, for example, as partial precipitation of the lime with alkali, or passage of ozone with the idea of oxidising humus. Wishing to try water of high chemical purity, I obtained—through the kind offices of Sir J. Dewar—water twice distilled from alkaline permanganate, and condensed in contact with silver, but the colour was no bluer. In the light of this evidence, I can hardly avoid the conclusion that the blueness of water in lengths of 4 metres has been exaggerated, especially by Spring, although I have no reason to doubt that a fully developed blue may be obtained at much greater thicknesses. I should suppose that sufficient care has not been taken to start with white light. It may be recalled that overcast days are not so common in some parts of the world as in England.

A third possible cause of apparent blueness of the sea must also be mentioned. If a liquid is not absolutely clear, but contains in suspension very minute particles, it will disperse light of a blue character. Although, undoubtedly, this cause must operate to some extent, I have seen no reason to think that it is important. But the existence of three possible causes of blueness complicates the interpretation of the phenomena. Hitherto observers have not been sufficiently upon their guard to distinguish blueness having its origin in the sky from blueness fairly attributable to the water itself.

As regards the light from the sky, the theory which attributes it to dispersal from small particles, many of which are smaller than the wave-length of light, is now pretty generally accepted. To a first

approximation at any rate, both the polarization and the colour of the light are easily explained. According to the simplest theory, the polarization should be absolute and a maximum at 90° from the sun, and the colour should be modified from that of the sun according to the factor λ^{-4}. But it is easy to see that there must be complications, even if all the particles are small and spherical. The light illuminating them is not merely the direct light of the sun, but also light diffused from the sky and from the earth's surface. On these grounds alone the polarization must be expected to be incomplete even at 90°, and the certain presence of particles not small in comparison with the wave-length is another cause operating in the same direction. It is rather remarkable that, as I noticed in 1871, the two polarised components show much the same colour. The observation is best made with a double-image prism mounted near one end of a pasteboard tube, through which a suitable rectangular aperture at the other end is seen double, but with the two images in close juxtaposition. When this is directed to a part of the sky 90° from the sun, and the tube turned until one image is at its darkest, the two polarised components are exhibited side by side in a manner favourable for comparison of colours. The addition at the eye end of a nicol capable of rotation independently of the tube, gives the means of equalising the brightnesses without altering the colours. This observation, made independently by Spring, is regarded by him as an objection to the theory, and as showing that the cause of the blueness and of the polarization are not the same. The argument would have more weight if the colours of the two components were exactly the same and under all circumstances, but I do not think that this is the case. Observations on the purer sky, to be seen from great elevations, would be of interest. The question is to what causes the second component is principally due. So far as it depends upon sky illumination, it would be bluer than the first component. Any "residual blue" of the kind described by Tyndall, and due to particles somewhat too big for the simple theory, would make a contribution in the same direction. On the other hand, large particles under the direct light of the sun, and perhaps small ones, so far as illuminated by light from the earth, would contribute a whiter light. In this way an approximate compensation may occur, but the matter is certainly worthy of further attention.

In this connection it should be noticed that, according to the now generally received electro-magnetic theory, complete polarization at 90° requires that the dispersing particles should behave as if spherical, even although infinitely small. If the shape be elongated, there would be incomplete polarization combined with similarity of colour even under the simplest conditions.

When the particles are no longer very small in comparison with the wave-length, the direction of maximum polarization was found

by Tyndall to become oblique, and the deviation is in the opposite direction to that which would have been anticipated from the Brewsterian law for the reflection of light from surfaces of finite area. As I showed in 1881, the gradual precipitation of sulphur from a very weak and acid solution of "hypo" exhibits the phenomena remarkably well. At a certain stage, depending on the colour of the light, the direction of maximum polarization becomes oblique. Even when the obliquity is well established for blue light, red light still continues to follow the simpler law, and the comparison gives curious information concerning the rate of growth of the particles.

The preferential scattering of light of short wave-length involves of course a gradual yellowing and ultimate reddening of the light transmitted. The formation in this way of sunset colours is well illustrated by the acid hypo.

That Spring rejects this theory in favour of one which would attribute sky-blue to absorption by oxygen or ozone, has been already alluded to. Although one must not conclude too hastily from the behaviour of these bodies when liquefied, it is, of course, possible that their absorbing qualities may influence atmospheric phenomena in some degree. But to attribute the blue of the sky to them seems out of the question. It is sufficient to remark that the setting sun turns red and not blue.

An interesting question remains behind. To what kind of small particles—dispersing short waves in preference—is the heavenly azure due ? That small particles of saline or other solid matter, including organic germs, play a part, cannot be doubted, and to them may be attributed much of the bluish haze by which the moderately distant landscape is often suffused. But it seems certain that the very molecules of air themselves are competent to scatter a blue light not very greatly inferior to that which we actually receive. Theory allows a connection to be established between the transparency of air for light of various wave-lengths, and its known refractivity in combination with Avagadro's constant, expressing the number of molecules per cubic centimetre in gas under standard atmospheric conditions. The first estimate of transparency was founded upon Maxwell's value of this constant, viz. $1 \cdot 9 \times 10^{19}$. Recent researches have shown that this number must be raised to $2 \cdot 76 \times 10^{19}$, and that the result is probably accurate to within a few per cent.* It has been pointed out by Dr. Schuster that the introduction of the raised number into the formula almost exactly accounts for the degree of atmospheric transparency observed at high elevations in the United States, apparently justifying to the full the inference that the normal blue of the sky is due to molecular scattering. But, although there is no

* It is a curious instance of divergence in scientific opinion that while some still deny the existence of molecules, others have successfully counted them.

reason to anticipate that this general conclusion will be upset, it should not be overlooked that a molecule, especially a diatomic molecule, can hardly be supposed to behave as if it were the dielectric sphere of theory. Questions are here suggested for whose decision the time is perhaps not yet ripe.

[R.]

P.S.—The question of the colour of the Mediterranean and other waters was long ago discussed by Mr. J. Aitken—an excellent observer—in Proc. Roy. Soc. Edin. 1881–82. His principal conclusions are very similar to my own. Mr. Aitken rightly insists upon the influence of the colour of the suspended matter to which the return of the light is due. Only when this is white, has the proper colour of the water a full chance of manifesting itself. From the heights of Capri, I noticed that the shallow water near the shore showed decidedly green, an effect attributed to the yellowness of the underlying sand.

Ionisation of Gases and Chemical Change.

THE term "catalytic" was introduced by Berzelius to describe a
number of chemical actions which would only take place in the
presence of a third substance, which itself was apparently unchanged
throughout the reaction. The first cases of such actions were inves-
tigated by Sir Humphry Davy in 1817. He showed that many
mixtures of gases were caused to unite in the presence of finely
divided platinum, at temperatures far below those at which union
ordinarily took place. Some years afterwards Faraday investigated
similar actions, and attempted to explain them by a supposed con-
densation of the gases on the surface of the metal.

Thirty years ago, Prof. H. B. Dixon investigated the behaviour
of carbon monoxide and oxygen when they were dried as completely
as possible, and he discovered that under these circumstances electric
sparks caused no explosion. Some years before, Wanklyn had dis-
covered that purified chlorine did not act on sodium, but he did
not identify the impurity, now known to be a trace of water, which
causes the vigorous action which takes place under ordinary circum-
stances.

In 1882 Cowper investigated the action of dried chlorine on
several metals, and found that the removal of moisture in many
cases inhibited the reaction.

In the following year, working in Prof. Dixon's laboratory at
Balliol College, I found that purified carbon could be heated to
redness in dried oxygen, and that sulphur and phosphorus could be
distilled in the same gas without burning. In the investigations
which followed, some thirty simple reactions have been tried by
myself and others. It has been shown that hydrogen and chlorine
can·be exposed to light without explosion, ammonia and hydrogen
chloride mixed without union, sulphur trioxide can be crystallised
on lime, ammonium chloride and mercurous chloride give undis-
sociated vapours, hydrogen and oxygen can be exposed to a red heat
without explosion, and lastly in 1907 nitrogen trioxide was obtained
as an undissociated gas for the first time by carefully drying the liquid,
and evaporating into a dried atmosphere.

The amount of water necessary to carry on these chemical reactions is extremely small, certainly less than 1 mg. in 300,000 litres. There is no accepted explanation of its catalytic effect, and in the same way the catalytic power of platinum is still a mystery. In 1893, Sir J. J. Thomson* showed that if the combination of atoms in a molecule is electrical in its nature, the presence of liquid drops of water, or drops of any liquid of high specific inductive capacity, would be sufficient to cause a loosening of the tie between the atoms, and this might result in chemical combination of the partially freed atoms to form new molecules. He showed in the same paper that drying a gas very completely stopped the passage of a current of 1200 volts. In the same year I was able in the same way to prevent the passage of discharge from an induction coil, a discharge which would traverse a spark gap of three times the distance in undried gas.

Shortly after the discovery of Röntgen rays it was found that they would ionise a gas through which they passed. At the time it was thought that this ionisation was similar to that taking place in electrolysis. If this were so the rays would probably cause chemical union to take place even in a dried gas, and accordingly Prof. Dixon and I undertook some experiments on the subject which were published in a joint paper.† The results were negative, no chemical action could be detected. Since that time the ionisation of gases has been shown to be of quite a different nature. The negative ion has been shown to be a particle of the mass of about $\frac{1}{1000}$th that of the hydrogen atom, and the positive ion is the residue. Since the ionisation of gases is different from that in electrolysis, the retention of this term is much to be deprecated. It is suggested that the term ionisation should be retained for electrolytic dissociation, and for the different process which takes place in gases under the action of Röntgen rays, etc., a new name, electromerism, should be adopted. The electron would thus be the negative electromer.

It is probable that electrolysis and true ionisation may take place in gases, as in the decomposition of steam by electric sparks of a particular length. An experiment, recently devised, seems to show that in mercury vapour, which ordinarily consists of atoms, something of the nature of ionisation without electrolysis can take place. If oxygen be admitted to the interior of a mercury lamp from which the current has just been cut off, a considerable quantity of mercuric oxide is produced, although the temperature of the lamp (about 150°) is far lower than would suffice to bring about the union of ordinary mercury vapour with oxygen.

In order to test further the question as to whether electromerism can bring about chemical change, I have investigated the action of radium bromide on very pure and dry hydrogen and oxygen. The gases were sealed up with some radium bromide contained in an

* Phil. Mag. xxxvi. 321.　　　† Chem. Soc. Jour. 1896.

open silica tube. The containing vessel was provided with a vacuum gauge, by means of which the combination of $\frac{1}{50000}$th part of the gases could be easily detected. No action whatever was observed, although the substances were left in contact for two months. A further experiment showed that, as was to be expected, very dry air undergoes electromerism when subjected to the action of radium. Two more tubes were then set up, similar to the first, containing mixtures of carbon monoxide and oxygen, one very dry, and the other containing traces of moisture, and although the radium bromide was in contact with them for more than three months not the slightest contraction could be observed. In these cases therefore electromerism produces no chemical change.

There, was, however, a possibility that electromerism might bring about a chemical action in a mixture of gases which was under conditions which were nearly, but not quite, suitable for chemical action to take place. The gaseous mixtures mentioned only combine, even when moist, at a red heat. Since the experiments were done at 20°, they only show that electromerism does not produce chemical action in gases which are otherwise unable to combine.

There remained the possibility that if gases were just on the point of combining, increasing the electromerism might accelerate the rate of action. I sought for a case of simple chemical union which would proceed at a manageable temperature, and at a rate which could be measured. Of those tried, the reaction between hydrogen and nitrous oxide was found to be the most suitable. The gases used were as pure as possible, but dried only by passing through phosphorus pentoxide tubes. They were found to combine with great uniformity when heated in clean Jena glass tubes to 530°. An electric resistance furnace was used, consisting of a wide silica tube which formed the heated chamber. It is known that many substances when heated, produce electromers in a gas; lime is fairly efficient, thoria more so, and, of course, radium bromide most of all. In the first experiment two tubes of the same Jena glass, containing the hydrogen and nitrous oxide mixture, were heated side by side. One contained some lime and in order to make the conditions as similar as possible, an equal quantity of powdered Jena glass was introduced into the other. As soon as the requisite temperature was reached, the action proceeded rapidly in the tube containing lime, the rate in the first five minutes being five times the rate of combination in the tube containing only powdered glass. After fifteen minutes the second tube had caught up the first, and the rates of union were equal up to the completion of the action. With thoria the effect was still more marked, the rate increasing to twenty times the rate in the tube containing the glass. Finally about 2 mg. of radium bromide was heated in the mixture of gases. As soon as the combining temperature was reached the gases in the radium bromide tube exploded.

From these three experiments it is seen that as the amount of

electromerism was increased, there was a rapid increase in chemical action.

I have recently been able to show that if the union of carbon monoxide and oxygen takes place in a strong electric field, which has the effect of removing electromers, the chemical action is diminished. Similar experiments are in progress with the mixture of hydrogen and chlorine, combining under the influence of light.

The next experiment tried, illustrates one way in which the electromerism of a gas may bring about chemical change. Hydrogen sulphide and sulphur dioxide can be mixed at the ordinary temperature in presence of traces of moisture, but in presence of liquid water, decomposition takes place into sulphur and water. The gases were dried before mixing by calcium chloride, which leaves about 4 mg. of water vapour per litre in the gas. After mixing, a small open silica tube containing about 2 mg. of dried radium bromide was introduced. After six hours no apparent change had taken place in the gas ; there was no deposit of sulphur on the sides of the jar, and it seemed at first as if no action had been produced. On opening the jar, however, an inrush of air was noticed, and the contents were almost odourless. On heating the radium tube a large quantity of water was driven off, and a copious sublimate of sulphur was seen. The whole of the gaseous contents of the jar had condensed in the small tube containing the radium bromide. The explanation of this action of radium bromide is probably simple. Water vapour condenses on the electromers emitted, liquid drops are formed, and in them the chemical action takes place.*

Prof. Townsend has recently published an account of some experiments, in which he has shown that there is a very marked decrease in the mobility of negative electromers in the presence of an amount of water vapour represented by a pressure of $\frac{1}{10}$th mm. The air, in his experiments, was subjected to the action of Röntgen rays.

It is concluded that water in a form approaching to that of a drop, is condensed on the electron even when a very small quantity is present. If this deposition of water molecules on electromers goes on when the amount of water present is still smaller, the theory of Sir J. J. Thomson affords a satisfactory explanation of the influence of moisture on chemical change, since some electromers are always present in ordinary gases.

[H. B. B.]

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* I have invariably noticed that water collects in tubes containing radium preparations exposed to undried air. The salts are not at all deliquescent, the crystals appearing quite sharp-edged under the microscope. I found that 10 mg. of radium bromide exposed to an atmosphere saturated at 0° for two days caused a deposition of water on its surface weighing 1·5 mg.

Friday, March 18, 1910.

SIR JAMES CRICHTON-BROWNE, M.D. LL.D. D.Sc. F.R.S.,
Treasurer and Vice-President, in the Chair.

PROFESSOR SIR J. J. THOMSON, M.A. LL.D. D.Sc. F.R.S. *M.R.I.*,
Professor of Natural Philosophy, Royal Institution.

The Dynamics of a Golf Ball.

THERE are so many dynamical problems connected with golf that a discussion of the whole of them would occupy far more time than is at my disposal this evening. I shall not attempt to deal with the many important questions which arise when we consider the impact of the club with the ball, but confine myself to the consideration of the flight of the ball after it has left the club. This problem is in any case a very interesting one, it would be even more interesting if we could accept the explanations of the behaviour of the ball given by many contributors to the very voluminous literature which has collected round the game ; if these were correct, I should have to bring before you this evening a new dynamics, and announce that matter when made up into golf balls obeys laws of an entirely different character from those governing its action when in any other condition.

If we could send off the ball from the club, as we might from a catapult, without spin, its behaviour would be regular, but uninteresting ; in the absence of wind its path would keep in a vertical plane, it would not deviate either to the right or to the left, and would fall to the ground after a comparatively short carry.

But a golf ball when it leaves the club is only in rare cases devoid of spin, and it is spin which gives the interest, variety, and vivacity to the flight of the ball. It is spin which accounts for the behaviour of a sliced or pulled ball, it is spin which makes the ball soar or "douk," or execute those wild flourishes which give the impression that the ball is endowed with an artistic temperament, and performs these eccentricities as an acrobat might throw in an extra somersault or two for the fun of the thing. This view, however, gives an entirely wrong impression of the temperament of a golf ball, which is in reality the most prosaic of things, knowing while in the air only one rule of conduct, which it obeys with unintelligent conscientiousness, that of always following its nose. This rule is the key to the behaviour of all balls when in the air, whether they are golf balls, base balls, cricket balls, or tennis balls. Let us, before entering into

the reason for this rule, trace out some of its consequences. By the nose of the ball we mean the point on the ball furthest in front. Thus if, as in Fig. 1, C the centre of the ball is moving horizontally to the right, A will be the nose of the ball ; if it is moving horizon-

FIG. 1.

tally to the left, B will be the nose. If it is moving in an inclined direction C P, as in Fig. 2, then A will be the nose.

Now let the ball have a spin on it about a horizontal axis, and suppose the ball is travelling horizontally as in Fig. 3, and that the
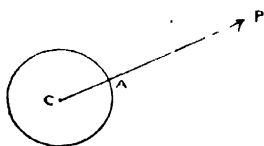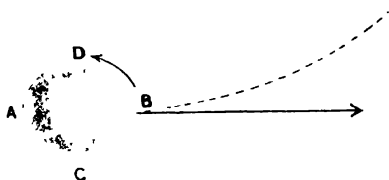

FIG. 2.   FIG. 3.

direction of the spin is as in the figure, then the nose A of the ball is moving upwards, and since by our rule the ball tries to follow its nose, the ball will rise and the path of the ball will be curved as in the dotted line. If the spin on the ball, still about a horizontal axis,
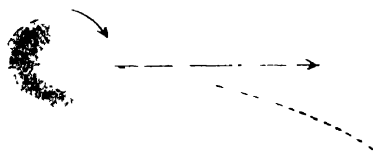

FIG. 4.

were in the opposite direction as in Fig. 4, then the nose A of the ball would be moving downwards, and as the ball tries to follow its nose it will duck downwards, and its path will be like the dotted line in Fig. 4.

Let us now suppose that the ball is spinning about a vertical axis, then if the spin is as in Fig. 5, as we look along the direction of the

flight of the ball the nose is moving to the right ; hence by our rule the ball will move off to the right, and its path will resemble the dotted line in Fig. 5, in fact, the ball will behave like a sliced ball. Such a ball, as a matter of fact, has spin of this kind about a vertical axis.

If the ball spins about a vertical axis in the opposite direction as in Fig. 6, then, looking along the line of flight, the nose is moving to the left, hence the ball moves off to the left, describing the path
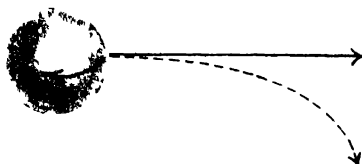

Fig. 5.

indicated by the dotted line ; this is the spin possessed by a "pulled" ball.

If the ball were spinning about an axis along the line of flight, the axis of spin would pass through the nose of the ball, and the spin would not affect the motion of the nose ; the ball following its nose would thus move on without deviation.

Thus, if a cricket ball were spinning about an axis parallel to the line joining the wickets, it would not swerve in the air, it would, however, break in one way or the other after striking the ground ; if, on the other hand, the ball were spinning about a vertical axis, it
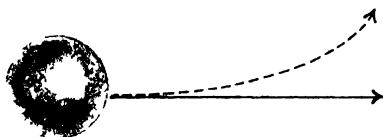

Fig. 6.

would swerve while in the air, but would not break on hitting the ground. If the ball were spinning about an axis intermediate between these directions it would both swerve and break.

Excellent examples of the effect of spin on the flight of a ball in the air are afforded in the game of base ball; an expert pitcher by putting on the appropriate spins can make the ball curve either to the right or to the left, upwards or downwards ; for the sideway curves the spin must be about a vertical axis, for the upward or downward ones about a horizontal axis.

A lawn-tennis player avails himself of the effect of spin when he puts "top spin" on his drives, i.e., hits the ball on the top so as to make it spin about a horizontal axis, the nose of the ball travelling

downwards as in Fig. 4 ; this makes the ball fall more quickly than it otherwise would, and thus tends to prevent it going out of the court.

Before proceeding to the explanation of this effect of spin I will show some experiments which illustrate the point we are considering. As the forces acting on the ball depend on the *relative* motion of the ball and the air, they will not be altered by superposing the same velocity on the air and the ball ; thus, suppose the ball is rushing forward through the air with the velocity V, the forces will be the same if we superpose on both air and ball a velocity equal and opposite to that of the ball ; the effect of this is to reduce the centre of the ball to rest, but to make the air rush past the ball as a wind moving with the velocity V. Thus, the forces are the same when the ball is moving and the air at rest, or when the ball is at rest and the air moving. In lecture experiments it is not convenient to have the ball flying about the room, it is much more convenient to keep the ball still and make the air move.

The first experiment I shall try is one made by Magnus in 1852 ; its object is to show that a rotating body moving relatively to the air
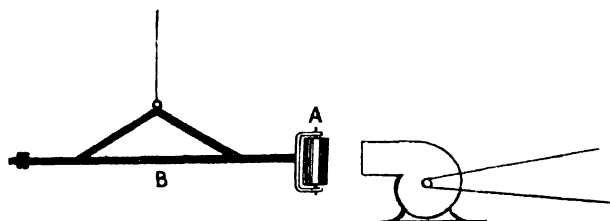

FIG. 7.

is acted on by a force in the direction in which the nose of the body is moving relatively to its centre : the direction of this force is thus at right angles, both to the direction in which the centre of the body is moving, and also to the axis about which the body is spinning. For this purpose a cylinder A (Fig. 7) is mounted on bearings so that it can be spun rapidly about a vertical axis ; the cylinder is attached to one end of the beam B, which is weighted at the other end, so that when the beam is suspended by a wire it takes up a horizontal position. The beam yields readily to any horizontal force, so that if the cylinder is acted on by such a force, this will be indicated by the motion of the beam. In front of the cylinder there is a pipe D, through which a rotating fan driven by an electric motor sends a blast of air which can be directed against the cylinder. I adjust the beam and the beam carrying the cylinder, so that the blast of air strikes the cylinder symmetrically ; in this case, when the cylinder is not rotating the impact against it of the stream of air does not give rise to any motion of the beam. I now spin the cylinder, and you see that when the blast strikes against it the beam moves off sideways. It goes off

one way when the spin is in one direction, and in the opposite way when the direction of spin is reversed. The beam, as you will see, rotates in the same direction as the cylinder, which an inspection of Fig. 8 will show you is just what it would do if the cylinder were acted upon by a force in the direction in which its nose (which, in this case, is
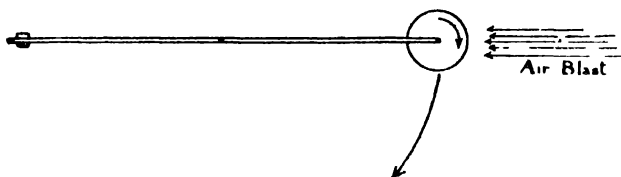

Fig. 8.

the point on the cylinder first struck by the blast) is moving. If I stop the blast, the beam does not move even though I spin the cylinder, nor does it move when the blast is in action if the rotation of the cylinder is stopped ; thus both spin of the cylinder and movement of it through the air are required to develop the force on the cylinder.
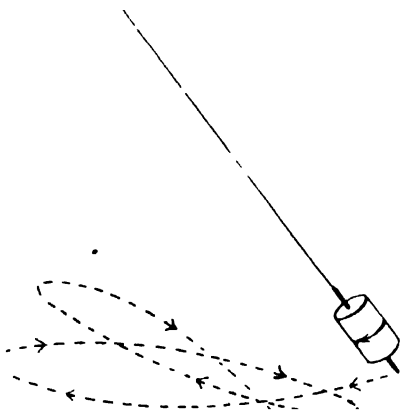
Fig. 9.

Another way of showing the existence of this force is to take a pendulum whose bob is a cylinder, or some other symmetrical body, mounted so that it can be set in rapid rotation about a vertical axis. When the bob of the pendulum is not spinning the pendulum keeps swinging in one plane, but when the bob is set spinning the plane in which the pendulum swings no longer remains stationary, but rotates slowly in the same sense as the bob is spinning (Fig. 9).

We shall now pass on to the consideration of how these forces arise. They arise because when a rotating body is moving through the air the pressure of the air on one side of the body is not the same as that on the other : the pressures on the two sides do not balance, and thus the body is pushed away from the side where the pressure is greatest.

Thus, when a golf ball is moving through the air, spinning in the direction shown in Fig. 10, the pressure on the side A B C, where
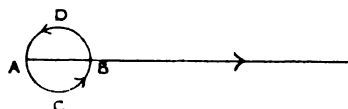

Fig. 10

the velocity due to the spin conspires with that of translation, is greater than that on the side A D B, where the velocity due to the spin is in the opposite direction to that due to the translatory motion of the ball through the air.

I will now try to show you an experiment which proves that this is the case, and also that the difference between the pressure on the two sides of the golf ball depends upon the roughness of the ball.
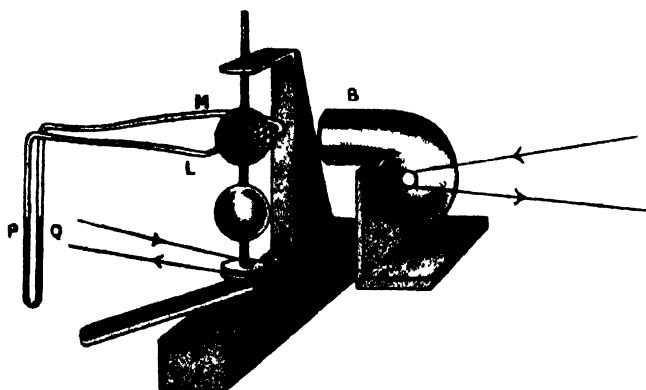

Fig. 11.

In this instrument, Fig. 11, two golf-balls, one smooth and the other having the ordinary bramble markings, are mounted on an axis, and can be set in rapid rotation by an electric motor. An air-blast produced by a fan comes through the pipe B, and can be directed against the balls; the instrument is provided with an arrangement by which the supports of the axis carrying the balls

can be raised or lowered so as to bring either the smooth or the bramble-marked ball opposite to the blast. The pressure is measured in the following way : L M are two tubes connected with the pressure-gauge P Q ; L and M are placed so that the golf balls can just fit in between them ; if the pressure of the air on the side M of the balls is greater than that of the side L the liquid on the right-hand side Q of the pressure-gauge will be depressed ; if, on the other hand, the pressure at L is greater than that at M the left-hand side P of the gauge will be depressed.

I first show that when the golf balls are not rotating there is no difference in the pressure on the two sides when the blast is directed against the balls : you see there is no motion of the liquid in the gauge. Next I stop the blast and make the golf balls rotate ; again there is no motion in the gauge. Now when the golf balls are spinning in the direction indicated in Fig. 11, I turn on the blast, the liquid falls on the side Q of the gauge, rises on the other side. Now I reverse the direction of rotation of the balls, and you see the motion of the liquid in the gauge is reversed, indicating that the high pressure has gone from one side to the other. You see that the pressure is higher on the side M where the spin carries this side of the ball into the blast, than on L where the spin tends to carry the ball away from the blast. If we could imagine ourselves on the golf ball, the wind would be stronger on the side M than on L, and it is on the side of the strong wind that the pressure is greatest. The case when the ball is still and the air moving from right to left is the same from the dynamical point of view as when the air is still and the ball moves from left to right ; hence we see that the pressure is greatest on the side where the spin makes the velocity through the air greater than it would be without spin.

Thus, if the golf ball is moving as in Fig. 12, the spin increases the pressure on the right of the ball, and diminishes the pressure on the left.

To show the difference between the smooth ball and the rough one, I bring the smooth ball opposite the blast ; you observe the difference between the levels of the liquid in the two arms of the gauge. I now move the rough ball into the place previously occupied by the smooth one, and you see that the difference of the levels is more than doubled, showing that with the same spin and speed of air blast the difference of pressure for the rough ball is more than twice that for the smooth.

FIG. 12.

We must now go on to consider why the pressure of the air on the two sides of the rotating ball should be different. The gist of the explanation was given by Newton nearly 250 years ago. Writing to Oldenburg in 1671 about the dispersion of light, he says, in the course of his letter, " I remembered that I had often seen a tennis-
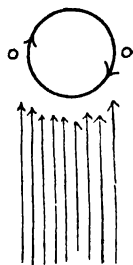
ball struck with an oblique racket describe such a curved line. For a circular as well as progressive motion being communicated to it by that stroke, its parts on that side where the motions conspire must press and beat the contiguous air more violently, and there excite a reluctancy and reaction of the air proportionately greater." This letter has more than a scientific interest—it shows that Newton set an excellent precedent to succeeding mathematicians and physicists by taking an interest in games. The same explanation was given by Magnus, and the mathematical theory of the effect is given by Lord Rayleigh in his paper on "The Irregular Flight of a Tennis-Ball," published in the 'Messenger of Mathematics,' vol vi. p. 14, 1877. Lord Rayleigh shows that the force on the ball resulting from this pressure difference is at right angles to the direction of motion of the ball, and also to the axis of spin, and that the magnitude of the force is proportioned to the velocity of the ball multiplied by the velocity of spin, multiplied by the sine of the angle between the direction of motion of the ball and the axis of spin. The analytical investigation of the effects which a force of this type would produce on the movement of a golf ball has been discussed very fully by Professor Tait, who also made a very interesting series
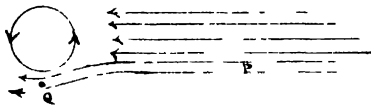

FIG. 13.

of experiments on the velocities and spin of golf balls when driven from the tee and the resistance they experience when moving through the air.

As I am afraid I cannot assume that all my hearers are expert mathematicians, I must endeavour to give a general explanation without using symbols, of how this difference of pressure is established.

Let us consider a golf-ball, Fig. 13, rotating in a current of air flowing past it. The air on the lower side of the ball will have its motion checked by the rotation of the ball, and will thus in the neighbourhood of the ball move more slowly than it would do if there were no golf ball present, or than it would do if the golf ball were there but was not spinning. Thus if we consider a stream of air flowing along the channel P Q, its velocity when near the ball at Q must be less than its velocity when it started at P; there must, then, have been pressure acting against the motion of the air as it moved from P to Q, i.e., the pressure of the air at Q must be greater than at a place like P, which is some distance from the ball. Now let us consider the other side of the ball : here the spin tends to carry the ball in the direction of the blast of air ; if the velocity of the surface of the ball is greater than that of the blast, the ball will

increase the velocity of the blast on this side, and if the velocity of the ball is less than that of the blast, though it will diminish the velocity of the air, it will not do so to so great an extent as on the other side of the ball. Thus the increase in pressure of the air at the top of the ball over that at P, if it exists at all, will be less than the increase in pressure at the bottom of the ball. Thus the pressure at the bottom of the ball will be greater than that at the top, so that the ball will be acted on by a force tending to make it move upwards.

We have supposed here that the golf ball is at rest, and the air rushing past it from right to left; the forces are just the same as if the air were at rest, and the golf ball rushing through it from left to right. As in Fig. 13, such a ball rotating in the direction shown in the figure will move upwards, i.e., it will follow its nose.

It may perhaps make the explanation of this difference of pressure easier if we take a somewhat commonplace example of a similar effect. Instead of a golf ball, let us consider the case of an Atlantic liner, and, to imitate the rotation of the ball, let us suppose that the passengers are taking their morning walk on the promenade deck, all circulating round the same way. When they are on one side of the boat they have to face the wind, on the other side they have the wind at their backs. Now when they face the wind, the pressure of the wind against them is greater than if they were at rest, and this increased pressure is exerted in all directions, and so acts against the part of the ship adjacent to the deck; when they are moving with their backs to the wind, the pressure against their backs is not so great as when they were still, so the pressure acting against this side of the ship will not be so great. Thus the rotation of the passengers will increase the pressure on the side of the ship when they are facing the wind, and diminish it on the other side. This case is quite analogous to that of the golf ball.

The difference between the pressures on the two sides of the golf ball is proportional to the velocity of the ball multiplied by the velocity of spin. As the spin imparted to the ball by a club with a given loft is proportional to the velocity with which the ball leaves the club ; the difference of pressure when the ball starts is proportional to the square of its initial velocity. The difference between the average pressures on the two sides of the ball need only be about one-fifth of one per cent. of the atmospheric pressure to produce a force on the ball greater than its weight. The ball leaves the club in a good drive with a velocity sufficient to produce far greater pressures than this. The consequence is that when the ball starts from the tee spinning in the direction shown in Fig. 14, this is often called underspin, the upward force due to the spin is greater than its weight, thus the resultant force is upwards, and the ball is repelled from the earth instead of being attracted to it. The consequence is that the path of the ball curves upward as in the curve A, instead of downwards as

in B, which would be its path if it had no spin. The spinning golf ball is in fact a very efficient heavier than air flying machine, the lifting force may be many times the weight of the ball.

The path of the golf ball takes very many interesting forms as the amount of spin changes. We can trace all these changes in the arrangement which I have here, and which I might call an electric golf links. With this apparatus I can subject small particles to forces of exactly the same type as those which act on a spinning golf ball.
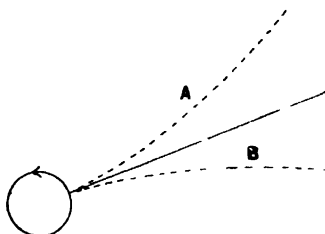
Fɪɢ. 14.

These particles start from what may be called the tee A (Fig. 15). This is a red hot piece of platinum with a spot of barium oxide upon it, the platinum is connected with an electric battery which causes negatively electrified particles to fly off the barium and travel down the glass tube in which the platinum strip is contained : nearly all the air has been exhausted from this tube. These particles are luminous, so that the path they take is very easily observed. We have now got our
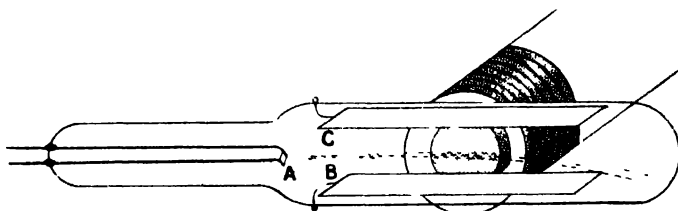
Fɪɢ. 15.

golf balls off from the tee, we must now introduce a vertical force to act upon them to correspond to the force of gravity on the golf ball. This is easily done by the horizontal plates B C, which are electrified by connecting them with an electric battery; the upper one is electrified negatively, hence when one of these particles moves between the plates it is exposed to a constant downwards force, quite analogous to the weight of the ball. You see now when the particles pass between the plates their path has the shape shown in

Fig. 16 ; this is the path of a ball without spin. I can imitate the effect of spin by exposing the particles while they are moving to magnetic force, for the theory of these particles shows that when a magnetic force acts upon them, it produces a mechanical force which is at right angles to the direction of motion of the particles, at right angles
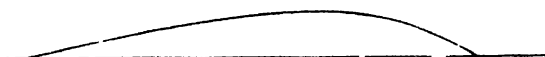
FIG. 16.

also to the magnetic force and proportional to the product of the velocity of the particles, the magnetic force and the sine of the angle between them. We have seen that the force acting on the golf ball is at right angles to the direction in which it is moving at right angles to the axis of spin, and proportional to the product of the velocity of
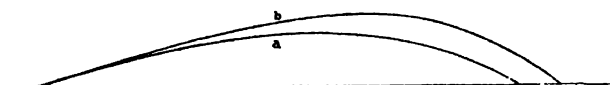
FIG 17

the ball, the velocity of spin and the sine of the angle between the velocity and the axis of spin. Comparing these statements you will see that the force on the particle is of the same type as that on the golf ball if the direction of the magnetic force is along the axis of spin and the magnitude of the force proportional to the velocity of spin,
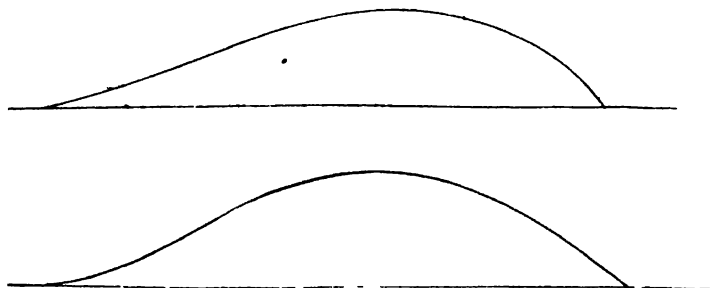
FIG. 18.

and thus if we watch the behaviour of these particles when under the magnetic force we shall get an indication of the behaviour of the spinning golf ball. Let us first consider the effect of under-spin on the flight of the ball : in this case the ball is spinning as in Fig. 3 about a horizontal axis at right angles to the direction of flight. To imitate this spin I must apply a horizontal magnetic force at right

angles to the direction of flight of the particles. I can do this by means of the electro-magnet I will begin with a weak magnetic force, representing a small spin. You see how the path differs from the one when there was no magnetic force ; the path, to begin with, is flatter though still concave, and the carry is greater than before —see Fig. 17, *a*. I now increase the strength of the magnetic field, and you will see that the carry is still further increased, Fig. 17, *b*. I increase the spin still furthei, and the initial path becomes convex instead of concave, with a still further inciease in carry, Fig. 18. Increasing the
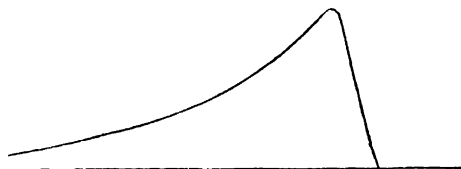
FIG. 19.

force still more, you see the particle soars to a great height, then comes suddenly down, the carry now being less than in the previous case (Fig. 19). This is still a familiar type of the path of the golf ball. I now increase the magnetic force still further, and now we get a type of flight not to my knowledge ever observed in a golf ball, but which would be produced if we could put on more spin than we are able to do at present. You see there is a kink in the curve, and at one part of the path the particle is actually travelling backwards (Fig. 20). Increasing the magnetic force I get more kinks, and we have a type

FIG. 20.
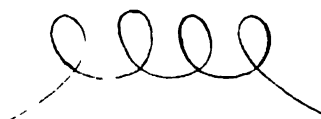
FIG. 21.

of drive which we have to leave to future generations of golfers to realise (Fig. 21).

By increasing the strength of the magnetic field I can make the curvature so great that the particles fly back behind the tee, as in Fig. 22.

So far I have been considering under-spin. Let us now illustrate slicing and pulling : in these cases the ball is spinning about a vertical axis. I must therefore move my electromagnet, and place it so that it produces a vertical magnetic force (Fig. 23). I make the force act one way, say downwards, and you see the particles curve

away to the right. behaving like a sliced ball.   I reverse the direction
of the force and make it act upwards, and the particles curve away to
the left, just like a pulled ball.

By increasing the magnetic force we can get slices and pulls much
more exuberant than even the worst we perpetrate on the links.

Though the kinks shown in Fig. 20 have never, as far as I am
aware, been observed on a golf-links, it is quite easy to produce them
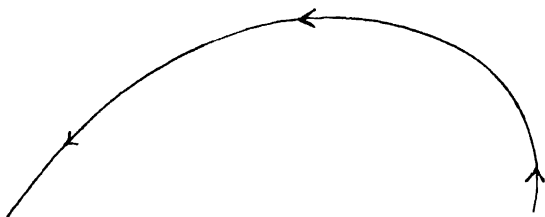
FIG 22.

if we use very light balls.   I have here a ball A made of very thin
india-rubber of the kind used for toy balloons, filled with air, and
weighing very little more than the air it displaces ; on striking this
with the hand, so as to put underspin upon it, you see that it describes
a loop, as in Fig. 24.

Striking the ball so as to make it spin about a vertical axis, you
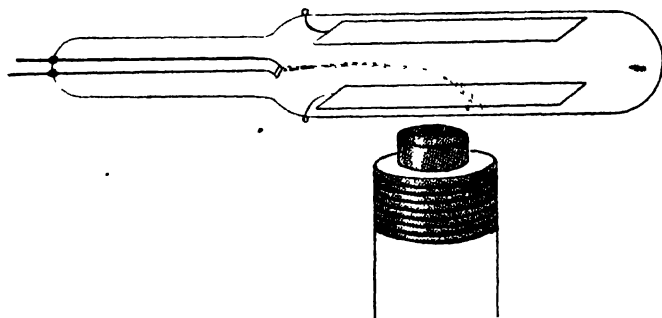
FIG. 23.

see that it moves off with a most exaggerated slice when its nose is
moving to the right looking at it from the tee, and with an equally
pronounced pull when its nose is moving to the left.

One very familiar property of slicing and pulling is that the
curvature due to them becomes much more pronounced when the
velocity of the ball has been reduced, than it was at the beginning
when the velocity was greatest.   We can easily understand why this

should be so if we consider the effect on the sideways motion of
reducing the velocity to one-half. Suppose a ball is projected from
A in the direction A B, but is sliced ; let us find the sideways motion
B C due to slice. The sideways force is, as we have seen, proportional
to the product of the velocity of the ball and the velocity of spin, or
if we keep the spin the same in the two cases, to the velocity of the
ball ; hence, if we halve the velocity we halve the sideways force,
hence, in the same time the displacement would be halved too, but
when the velocity is halved the time taken for the ball to pass from
A to B is doubled. Now the displacement produced by a constant
force is proportional to the square of the time ; hence, if the force
had remained constant, the sideways deflection B C would have been
increased four times by halving the velocity, but as halving the
velocity halves the force, B C is doubled when the velocity is halved ;
thus the sideways movement is twice as great when the velocity is
halved.
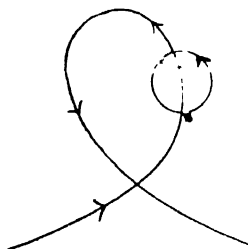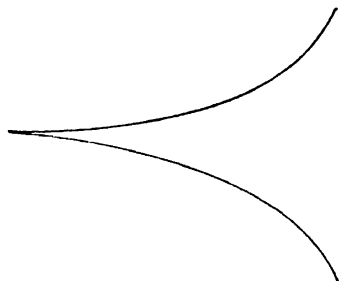
FIG. 24.   FIG. 25.

If the velocity of spin diminished as rapidly as that of translation
the curvature would not increase as the velocity diminished, but the
resistance of the air has more effect on the speed of the ball than on
its spin, so that the speed falls the more rapidly of the two.

The general effect of wind upon the motion of a spinning ball
can easily be deduced from the principles we discussed in the earlier
part of the lecture. Take, first, the case of a head-wind. This wind
increases the relative velocity of the ball with respect to the air ;
since the force due to the spin is proportional to this velocity, the
wind increases this force, so that the effects due to spin are more
pronounced when there is a head-wind than on a calm day. All golfers
must have had only too many opportunities of noticing this. Another
illustration is found in cricket ; many bowlers are able to swerve when
bowling against the wind who cannot do so to any considerable
extent on a calm day.

Let us now consider the effect of a cross-wind. Suppose the wind
is blowing from left to right, then, if the ball is pulled, it will be

rotating in the direction shown in Fig. 26 ; the rules we found for
the effect of rotation on the difference of pressure on the two sides
of a ball in a blast of air show that in this case the pressure on the
front half of the ball will be greater than that on the rear half, and
thus tend to stop the flight of the ball.   If, however, the spin was
that for a slice, the pressure on the rear half would be greater than
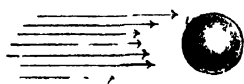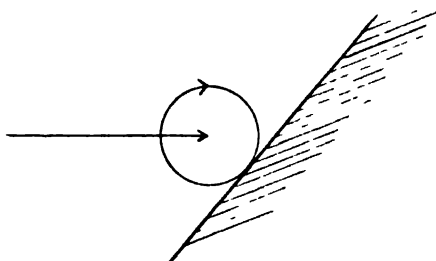
FIG. 26.   FIG. 27.

the pressure in front, so that the difference in pressure would tend to
push on the ball and make it travel further than it otherwise would.
The moral of this is that if the wind is coming from the left we
should play up into the wind and slice the ball, while if it is coming
from the right we should play up into it and pull the ball.

I have not time for more than a few words as to how the ball
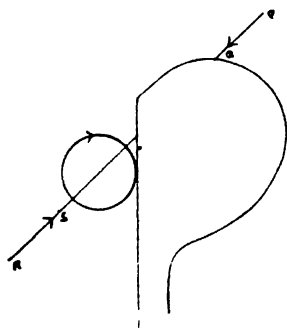
FIG. 28.   FIG. 29.

acquires the spin from the club.   But if you grasp the principle that
the action between the club and the ball depends only on their *relative*
motion, and that it is the same whether we have the ball fixed and
move the club, or have the club fixed and project the ball against it,
the main features are very easily understood.

Suppose Fig. 27 represents the section of the head of a lofted club

moving horizontally forward from right to left, the effect of the impact will be the same as if the club were at rest and the ball were shot against it horizontally from left to right. Evidently, however, in this case the ball would tend to roll up the face, and would thus get spin about a horizontal axis in the direction shown in the figure ; this is underspin, and produces the upward force which tends to increase the carry of the ball.

Suppose, now, the face of the club is not square to its direction of motion, but that looking down on the club its line of motion when it strikes the ball is along P Q (Fig. 28), such a motion as would be
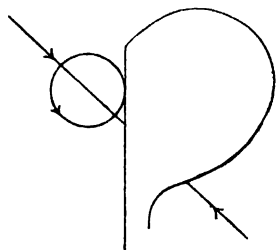
FIG. 30.

FIG. 31.

produced if the arms were pulled in at the end of the stroke, the effect of the impact now will be the same as if the club were at rest and the ball projected along R S, the ball will endeavour to roll along the face away from the striker ; it will spin in the direction shown in the figure about a vertical axis. This, as we have seen, is the spin which produces a slice. The same spin would be produced if the motion of the club was along L M and the face turned so as to be in the position shown in Fig. 29, i.e., with the heel in front of the toe.

If the motion and position of the club were as in Figs. 30 and 31, instead of as in Figs. 28 and 29, the same consideration would show that the spin would be that possessed by a pulled ball.

[J. J. T.]

Sir Francis Laking, Bart., G.C.V.O. M.D. LL.D.,
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The Chemical Significance of Crystal Structure.

Large numbers of chemical substances occur on the earth's surface as definite geometrical forms bounded by plane faces ; these polyhedral shapes are called crystals.   Inspection of the crystal forms assumed by mineral substances shows that, roughly speaking, each crystalline substance affects some specific geometrical shape which is characteristic for the material ; further that, whilst crystals of any particular mineral attain vastly different dimensions and are bounded by planes which vary greatly in relative area, one geometrical feature remains constant.   The angles between corresponding pairs of faces on any two crystals of the same substance are the same, notwithstanding the existence of difference in size, or in relative face magnitude between the two crystals.   The constancy of interfacial angle amongst crystals of the same substance is a law of nature, and has been amply demonstrated by the very careful crystallographic measurements made by Tutton during the last 20 years.

It is, however, not essential to study mineral substances alone in order to obtain a knowledge of the laws governing crystal growth. Great numbers of laboratory products can be caused to crystallise by condensation from some fluid condition ; thus, the crystals of various alums exhibited were obtained by slow evaporation of aqueous solutions of these salts.

The examination of a crystal shows that many of its physical properties differ according to the direction in the crystal in which the property is determined ; the hardness of crystals, the speed at which light travels through them, and many other properties, are commonly dependent on the direction in which the material is examined.

The dependence of crystal properties on direction indicates the most essential feature of the crystal to be a definite and orderly arrangement of its ultimate particles ; this arrangement is referred to as the crystal structure.   Further evidence that crystals possess an arranged structure is furnished by the observation that crystallisation is not necessarily a spontaneous process.   Thus, on melting benzophenone and rapidly cooling the clear molten mass, the liquid state is

retained for many hours at a temperature far below the normal melting point of the compound. But on inoculating the liquid with a trace of crystalline benzophenone crystallisation immediately commences and rapidly becomes complete. The introduction of a small particle of crystalline or arranged material into the liquid mass provides a nucleus upon which the molecules are able to deposit themselves in a similar crystalline arrangement; the process thus started quickly becomes propagated throughout the entire mass. The lack of spontaneity in the process of crystallisation leads occasionally to quite unexpected results. Thus, tetrahydroquinaldine has been known for many years, and has been prepared by numbers of chemists. It has always been obtained as a liquid, and has never been supposed capable of existing in the crystalline state at ordinary temperatures: even when cooled in liquid air it merely becomes a thick resin, and does not crystallise. But on dissolving a few drops of it in a little light petroleum and cooling the solution thus obtained in liquid air, the tetrahydroquinaldine crystallises out; on transferring a trace of the crystalline material obtained to the liquid substance at the ordinary temperature, the liquid mass is seen to immediately crystallise. This well-known substance, hitherto known only in the liquid state at ordinary temperatures, really exists in a more stable condition as a crystalline solid.

Many substances are capable of crystallising in two or more distinct crystalline forms of which one is, in general, the more stable at any particular temperature. The physical properties of the several crystalline modifications of any one substance are quite distinct and characteristic for the particular crystalline form and, in many instances, even the colours of the several modifications are different. An example of this is afforded by pouring boiling water into a beaker coated with cuprous mercuric iodide; the brilliant scarlet crystalline form stable at ordinary temperatures, when heated in this way, becomes converted into another crystalline modification which is nearly black. The change is a reversible one, and the differences between the properties of the two crystalline modifications are to be attributed to differences in the mode of arrangement of the molecules in the two cases; the two modifications, in fact, possess different crystalline structures.

Although vast numbers of observations, such as the preceding, lead to the conclusion that crystals are arranged structures, it is not essential that the crystal should be a solid substance; during recent years large numbers of crystalline liquids have been discovered. On allowing melted cholesteryl chloride to cool rapidly a brilliant display of interference colours is seen owing to the particles of the substance assuming crystalline or orderly arrangement whilst still retaining the liquid condition.

Having very briefly reviewed some of the many reasons for concluding that crystals are structured edifices, the nature of the architecture which they exhibit may now be considered. All the properties of crystalline solids harmonise with one simple assumption as to the

manner in which the parts of the structure are arranged ; this assumption is that the structure is a geometrically " homogeneous " one, that is, a structure the parts of which are uniformly repeated throughout, corresponding points having a similar environment everywhere within the edifice. The assumption of geometrical homogeneity as the characteristic of crystalline solids leads at once to the great problem solved by the crystallographers of the nineteenth century. This consisted in the inquiry as to how many types of homogeneous arrangement of points in space are possible, to the study of those types and to their identification, in symmetry and other respects, with the known systems into which crystalline solids fall. This work was commenced by the German crystallographer Frankenheim in 1830, and completed by the English geometrician Barlow in 1894. Briefly stated, the final conclusion has been attained that 230 geometrically homogeneous modes exist of distributing material, or points representing material throughout space, and that these 230 homogeneous types of structure, the so-called homogeneous " point-systems," fall into the 32 types of symmetry exhibited by crystalline solids. Models of a number of homogeneous point systems illustrating some of these types are exhibited.

It is, however, obvious that the limitation of the possibilities of solid crystalline arrangement to 230 types marks but one stage in the determination of the nature of crystal structure, and throws no direct light on the relation between crystal structure and chemical constitution. Although by the end of the nineteenth century we had learnt that corresponding points of the units of crystalline structures form homogeneous point-systems, the great problem still remained of determining what are the entities which become homogeneously arranged, for what reason they become so arranged, and in what way the conclusions drawn by modern chemistry are reflected in crystal structure. This problem was a legacy to the twentieth century, and it now remains to indicate briefly the extent to which it has been solved and the results of chemical importance which have accrued during its investigation.

The problem may be most easily visualised in connection with some comparatively simple case, that, for instance, presented by the crystalline forms assumed by the elements themselves. It is generally admitted that an elementary substance consists of identical atoms, each of which acts as a centre of operation of attractive and repulsive forces. In a solid crystalline structure the atoms are obviously not free to travel through the mass, each, if not indeed fixed to a particular spot, being retained within a certain minute domain ; each of these domains must be regarded as possessing a centre which marks the mean position of the atom.

The crystalline condition of an element may consequently be defined as one of equilibrium between forces of attraction and repulsion emanating from or referable to a flock of points homogeneously

arranged in space, that is to say, of points of a homogeneous point-system. Under these conditions, the space occupied by a crystalline element, a homogeneous assemblage of identically similar atoms, may be partitioned into identically similar cells in such a manner that the boundaries of a single cell shall enclose the entire domain throughout which a particular atom exercises predominant influence. Since it is postulated that every point in the space is subject to the dominating influence of some next neighbouring atomic centre, it follows that the cells fit together so as to occupy the whole available space without interstices. Nothing is here said about the shape of
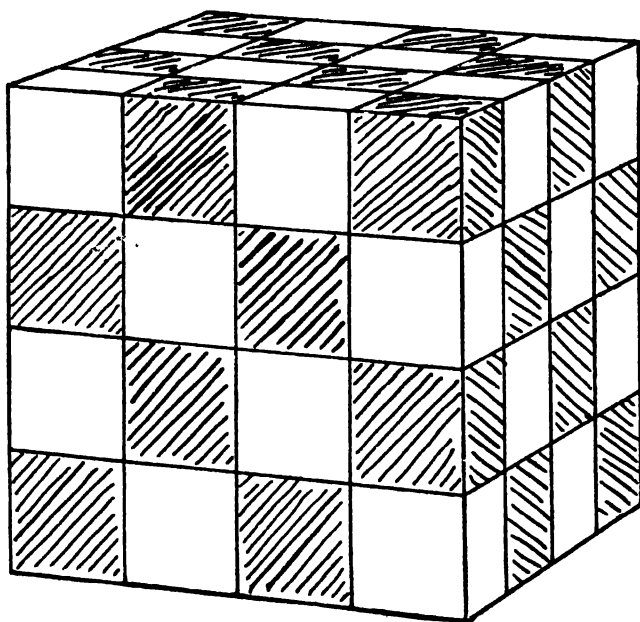
FIG. 1.

the cells; but, since, in the case of an elementary substance, the atomic centres are all alike, so too will be the cells. Before proceeding to discuss the actual shapes of the cells referred to, it will be convenient to illustrate more graphically the mode of treating the problem which is here introduced with the aid of a particular point-system connected with the crystalline structure of elementary substances.

The point-system in question may be derived in the following manner. Space is first partitioned into cubes by three sets of parallel planes at right angles to one another (Fig. 1); a point is then placed at each cube corner and at the centre of each cube face.
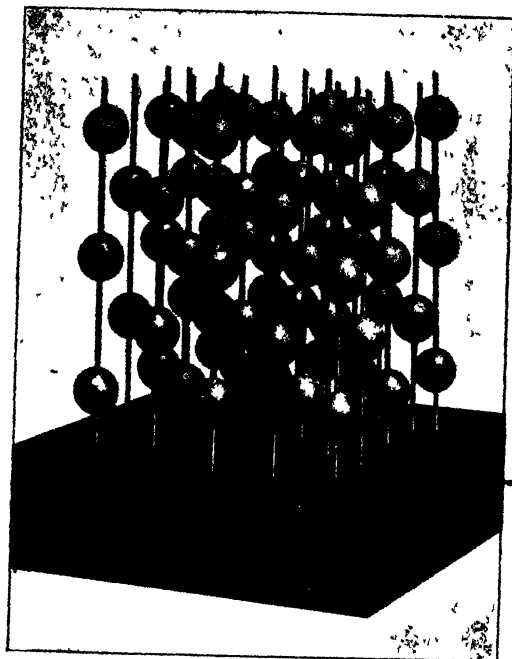
Fig. 2.
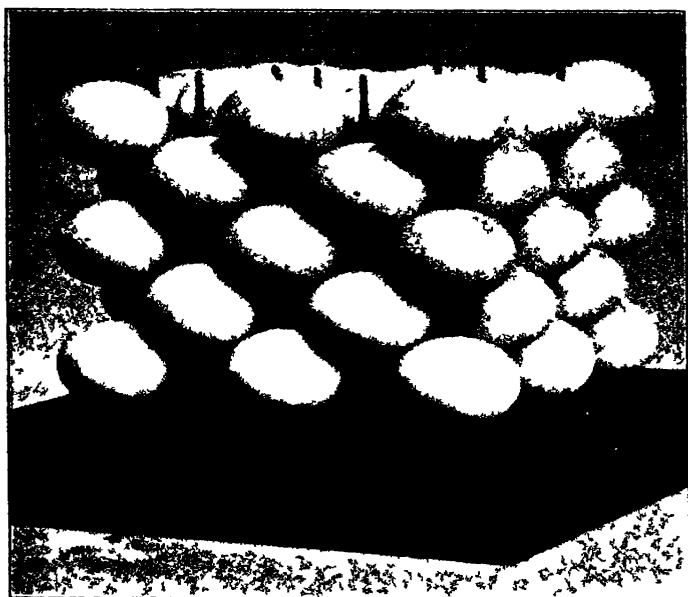
FIG. 3
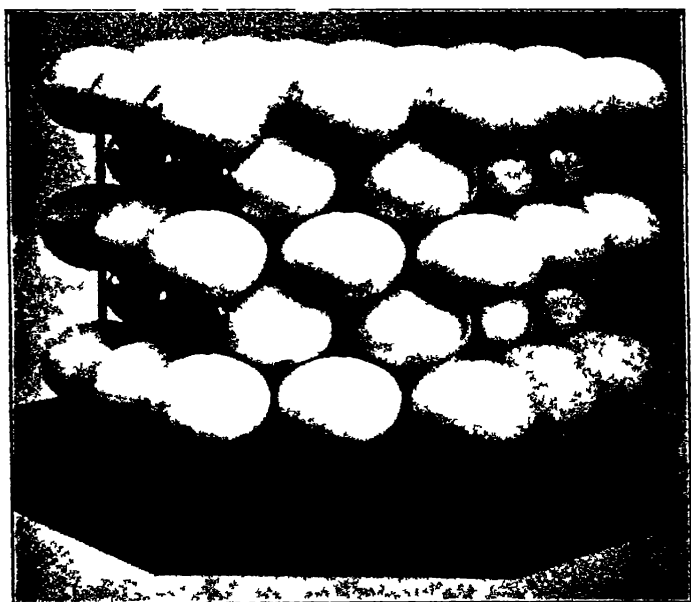
FIG. 4.

The cubes of the partitioning, having served their purpose, may now be removed, leaving one of the 230 types of homogeneous point-systems (Fig. 2). Imagine next that each point of the system expands uniformly in all directions until it touches its neighbours ; a system of spheres packed together in contact is thus obtained (Fig. 3), and, on examination, it is found that no way exists of packing these equal spheres more closely together than the one thus derived. The system is therefore termed the cubic closest-packed assemblage of equal spheres and, being derived in the manner described, still retains the high symmetry of the cube ; the fragment shown, in fact, outlines a cube. Three directions at right angles in it, those which are parallel to the three cube edges, are seen to be identical in kind ; this identity in kind in the three rectangular directions, a, b and c, is conveniently expressed by the ratio, $a : b : c = 1 : 1 : 1$.

On removing spheres from one corner of the cubic closest-packed assemblage of equal spheres a close triangularly arranged layer is disclosed, and, by similarly treating each corner of the fragment of assemblage, the cube outline gives place to one of octahedral form. The assemblage is now seen to be built up by the superposition of the disclosed triangularly arranged layers, the hollows in one layer serving to accommodate the projecting parts of the spheres in adjacent layers. When this operation is performed it is perceived, however, that two ways of stacking the layers homogeneously are possible. The first of these, in which the fourth layer lies immediately over the first, the fifth over the second, and so on, yields the cubic closest-packed assemblage. The alternative mode of stacking, in which the third layer lies immediately over the first, the fourth over the second, and so on, exhibits the same closeness of packing as the first, but possesses the symmetry of the hexagonal crystal system ; it is accordingly termed the hexagonal closest-packed assemblage of equal spheres (Fig. 4). Examination of the hexagonal assemblage shows that the horizontal directions, in the planes of the layers, are not identical in kind with vertical directions, perpendicular to the planes of the layers. Corresponding dimensions in these two directions, a and c, are in the ratio of

$$a : c = 1 : \sqrt{(\tfrac{2}{3})} = 1 : 0\cdot 8165.$$

The final step in the treatment of the closest-packed assemblages of equal spheres consists in converting them into the corresponding assemblages of cells fitting together without interstices which have been already mentioned ; it may be carried out in these, and in all other cases, by causing the component spheres to expand uniformly in all directions until expansion is checked by contact with the expanding parts of neighbouring spheres. The cubic closest-packed assemblage then becomes a stack of twelve-sided polyhedra, rhombic dodecahedra, which are so fitted together as to fill space without interstices. It is

now seen that the even rate of expansion from each point of the original point-system which gives rise to the closely packed stack of rhombic dodecahedra, symbolises an even radiation in all directions of the forces of which the atom is the centre of emanation. On applying the same operation of expansion to the spheres present in hexagonal closest-packing, each becomes converted into a dodeca-hedron, although of symmetry different from that of the rhombic dodecahedron. In each of the two cases the system exhibits the important property that, with a given density of distribution of the centres, a maximum distance prevails between nearest centres; these two systems thus represent the equilibrium arrangements of the postu-lated forces of repulsion exerted between near centres, the repulsions between more distant ones being neglected.

It will be sufficiently evident from what has been said that the function of the spherical surfaces in the closest-packed assemblages of spheres, as representing crystal structures, is merely a geometrical one; these surfaces are employed only as so much scaffolding by the aid of which may be derived arrangements exhibiting a maximum number of equal distances between neighbouring centres, and no phy-sical distinction is to be made between portions of space lying within the spheres and portions forming part of the interstices between them. Insistence on this point is necessary, because many investigators have made use, quite illegitimately, of spheres for the representation of atomic domains, piling the spheres together in what they have termed open packing; this term seems to imply that some physical difference can subsist between the portions of space lying within the spheres and those lying without. The one kind of space is apparently regarded as susceptible to atomic influence in some sense not exhibited by the other. To state this view in any definite manner probably suffices to demonstrate its superficiality: the question of ascertaining what pro-portion of the total space is available for atomic occupation by the use of assemblages of spheres does not arise because the spheres used are solely the geometrical instruments for producing equality amongst the atomic distances, and so determining the prevailing equilibrium conditions.

So far as the enquiry has been carried, it would seem that the elements should crystallise either in the cubic or the hexagonal system, and that in the latter case corresponding dimensions in the horizontal and vertical directions should be in the ratio of $a : c = 1 : 0\cdot8165$. The facts are summarised in Table I.

Of the elements which have been crystallographically examined, 50 per cent. are cubic; their crystal structure is simulated by the cubic closest-packed assemblage of equal spheres. Another 35 per ·cent. belong to the hexagonal system, and that these are correctly represented by the hexagonal closest-packed assemblage of equal spheres is indicated by the fact that for the hexagonal elements, the ratio of corresponding dimensions in the horizontal and vertical direc-

tions approximates to the value $a : c = 1 : 0\cdot8165$, deduced for the model assemblage.

The task of accounting for the 15 per cent. of the crystalline elements which have been examined and found to crystallise in systems

TABLE I.—RELATION BETWEEN CRYSTAL FORM AND MOLECULAR
COMPLEXITY.

Crystal System.	Elements.	Number of Atoms in Molecules of Compound Inorganic Substances.					Organic Compounds
		2	3	4	5	More than 5	
Cubic	50	68·5	42	5	12	5·8	2·5
Hexagonal . . .	35	19·5	11	35	38	14·6	4·0
Tetragonal . . .	5	4·5	19	5	6	7	5·0
Orthorhombic . . .	5	3·0	23·5	50	36	27·3	34·0
Monosymmetric . .	5	4·5	3	5	6	37·3	47·5
Anorthic	0	0	1·5	0	2	8	7·0
Number of cases summarised in each vertical column . . .	40	67	63	20	50	673	585

The proportion of substances crystallising in each system is stated
above as a percentage.

other than the cubic or hexagonal still remains. A little inspection shows that the crystal forms of these elements in every case approach very closely to one or other of the two of highest symmetry, namely the cubic or the hexagonal ; one example of this will now suffice. The values of corresponding dimensions in three directions in space for the monosymmetric form of the element sulphur are given by the axial ratios $a : b : c = 0\cdot9958 : 1 : 0\cdot9998$, $\beta = 95^\circ 46'$. The slight departure of these dimensions from the corresponding values for the cubic closest-packed assemblage, in which $a : b : c = 1 : 1 : 1$, $\beta = 90^\circ$, at once suggests that the monosymmetric modification of sulphur is derived from the latter assemblage by some minute distortion. Such a distortion indicates a very trifling departure from uniformity in the influence exerted in different directions from each atomic centre, and may either arise from some want of symmetry in the individual atoms, or in a reduction of the symmetry caused by some grouping of the atoms ; two or more atoms might thus be more closely connected in some way with one another than with other next neighbouring atoms.

Having shown that the crystalline forms of the elements are in complete harmony with the conception that crystal structures can be homogeneously divided into similar cells of polyhedral shapes approximating closely to the spherical, reference may now be made to some simple compounds, those, namely, in which the molecule consists of two dissimilar atoms.

The conception of the equilibrium of centred forces which has

been shown fertile in the case of the crystalline elements can be immediately applied to the binary compounds ; as before, each atom will be represented by forces emanating from a centre, and equilibrium will demand closest packing of the spheres used, just as in the previous case.   The atomic centres will now, however, be of two kinds, and the question arises as to whether the domains of atomic influence to be described about them will be all of the same magnitude or whether two magnitudes of spheres must be employed, one for each element present.   This question is difficult to answer by reference to the facts already reviewed above ; probably the only indication which the latter afford in this connection is that closest-packing of a considerable variety of different magnitudes would certainly be most unlikely to lead to the close similarity of crystal form observed as between the elements and the binary compounds.   A direct answer is, however, provided as the result of investigating the crystalline forms of organic substances, to which reference will presently be made ; this investigation has led to the discovery of a definite law which governs the magnitudes of the several kinds of atomic domain concerned in any crystalline compound substance. It is found that the magnitudes of the atomic domains in any crystalline compound are very approximately in the ratio indicated by the fundamental valencies of the corresponding elements.   Since the molecules of nearly all the binary compounds which have been crystallographically examined contain in the molecule one atom each of two elements of the same valency, the polyhedral cells from which a crystalline binary compound must be supposed built up are all, in general, of approximately the same magnitude.   The fact that most binary compounds, like most elements, crystallise in either the cubic or the hexagonal system, represents one of the simple results of this law of valency volumes.

The binary compounds thus, in general, affect crystalline structures which are derived from the cubic or the hexagonal closest-packed assemblage of equal spheres ; one-half of the spheres, selected homogeneously, represent atoms of the one element and the remainder atoms of the second element.   The mode in which the necessary homogeneous selection may be made in the cubic assemblage, without altering the values of corresponding dimensions in three rectangular directions, is shown in a model.

The crystalline forms of the binary compounds are in accordance with what has been above foreshadowed.   Table I. indicates that in geometrical respects the crystalline binary compounds closely resemble the elements ; 68·5 per cent. of those examined are cubic and 19·5 per cent. hexagonal, the remaining 12 per cent. crystallising in systems of lower symmetry than these.   The axial ratios, $a : c$, of all the hexagonal binary compounds known are stated in Table II.; all approximate closely to the value, $a : c = 1 : 0·8165$, for the model hexagonal closest-packed assemblage of equal spheres.

TABLE II.—HEXAGONAL BINARY COMPOUNDS.

					$a : c$
Beryllium oxide	.	BeO	.	.	$1 : 0\cdot8153$
Zinc oxide	.	.	ZnO	.	.	$1 : 0\cdot8039$
Zinc sulphide	.	.	ZnS	.	.	$1 : 0\cdot8175$
Cadmium sulphide	.	CdS	.	.	$1 : 0\cdot8109$
Silver iodide	.	.	AgI	.	.	$1 : 0\cdot8196$
The ratio, $1 : \sqrt{(\frac{2}{3})}$	.	.	.	.	$1 : 0\cdot8165$

In connection with the elements and binary compounds it is note-worthy that the mode of treatment described appears practically to eliminate molecular aggregation of the atoms as a factor in determin-ing the crystalline structure ; that is to say, the distance separating two neighbouring atom centres is the same whether those atoms belong to the same or to different molecules.   Another interest-ing fact is that, whilst the elements and binary compounds for the most part crystallise in the cubic or hexagonal systems, sub-stances of greater molecular complexity rarely crystallise in these highly symmetrical systems ; thus, of a great number of organic compounds examined, $2\cdot5$ and $4\cdot0$ per cent. only belong to the cubic and hexagonal crystalline systems respectively (Table I).   This observation is important as one of many indications that the cells into which the crystal structure of a complex compound are par-titionable are not, in general, all of the same volume.   Further in-vestigation shows that the volumes of the polyhedral cells representing the atomic domains of the several elements present in a complex crystal-line compound are governed by the law of valency volumes to which reference has already been made.   The correctness of this conclusion concerning the proportionality between the numbers expressing the fundamental valencies of the elements and the volumes of the corre-sponding spheres of atomic influence has been abundantly verified, not only by the laborious process of working out a large number of cases, but in several other ways which may be more rapidly indicated. The following are illustrations of the latter kind of verification.

Table III. states the composition and axial ratios, $a : b : c$, of a series of four crystalline minerals which differ in composition by the increment, Mg_2SiO_4 ; the sums of the valencies of the atoms composing the different molecular aggregates are stated under the heading, W.   The increment, Mg_2SiO_4, also occurs as the crystalline mineral forsterite, of which the axial ratios have been determined. It is evident that the ratio, a/b, has approximately the same value of $1\cdot08$ for all four members of the series, and that practically all differences in relative dimensions are expressed by the ratio, c/b. On dividing the valency volume, W, by the corresponding value for c/b in each case, the quotients $11\cdot7$, $12\cdot1$, $12\cdot3$, $12\cdot4$ and $12\cdot7$ are obtained respectively for the substances prolectite, chondrodite, humite, clinohumite, and forsterite.   The relative dimension, c/b, is thus roughly proportional to the sum of the valencies in this set of

minerals. The comparison may, however, be made more accurately by including the changes in both relative dimensions, a/b and c/b, in the calculation in the following manner. The "equivalence parameters" are the rectangular dimensions, x, y and z, of a rectangular block having the volume W, and are in the ratio of the axial ratios, $a : b : c$. The parameters x and y preserve almost constant values throughout the series, and addition of the increment, Mg_2SiO_4, leads to a practically constant increase of about $2 \cdot 86$ in the dimension z, on passing from one mineral to the next in the series. The mineral forsterite also gives nearly the same x and y values as before, and its z value, $2 \cdot 87$, is equal to the differences between consecutive pairs of z values in the main series ; these differences vary between $2 \cdot 85$ and $2 \cdot 88$. The axial ratios and equivalence parameters of forsterite can indeed be calculated with considerable accuracy from the data available for the series of four minerals.

<div align="center">TABLE III.—THE HUMITE MINERALS.</div>

Prolectite	.	$MgSiO_4$,	$2Mg(F,OH)$	.	W = 22
Chondrodite	.	$Mg_3(SiO_4)_2$,	$2Mg(F,OH)$	.	W = 38
Humite .	.	$Mg_5(SiO_4)_3$,	$2Mg(F,OH)$	.	W = 54
Clinohumite	.	$Mg_7(SiO_4)_4$,	$2Mg(F,OH)$	.	W = 70

The increment is Mg_2SiO_4, namely, forsterite, with W = 16.

	Axial Ratios.	Equivalence Parameters.
	$a\ :\ b :\ c$	$x\ :\ y\ :\ z$
Prolectite	. $1 \cdot 0803 : 1 : 1 \cdot 8862$	$2 \cdot 389 : 2 \cdot 210 :\ 4 \cdot 169$
		Diff. $= 2 \cdot 851$
Chondrodite	. $1 \cdot 0863 : 1 : 3 \cdot 1447$	$2 \cdot 425 : 2 \cdot 232 :\ 7 \cdot 020$
		Diff. $= 2 \cdot 877$
Humite .	. $1 \cdot 0802 : 1 : 4 \cdot 4033$	$2 \cdot 428 : 2 \cdot 247 :\ 9 \cdot 897$
		Diff. $= 2 \cdot 858$
Clinohumite	. $1 \cdot 0803 : 1 : 5 \cdot 6588$	$2 \cdot 435 : 2 \cdot 254 : 12 \cdot 755$

<div align="center">Values for the increment, forsterite.</div>

Observed .	. $1 \cdot 0757 : 1 : 1 \cdot 2601$	$2 \cdot 449 : 2 \cdot 277 :\ 2 \cdot 869$
Calculated	. $1 \cdot 0823 : 1 : 1 \cdot 2775$	$2 \cdot 429 : 2 \cdot 245 :\ 2 \cdot 867$

The relations here displayed may be rendered more obvious by a series of models (Fig. 5). Rectangular blocks having as the horizontal dimensions the x and y values, and as vertical dimension the z value, for forsterite, when superposed upon a similar set of blocks having the corresponding dimensions for prolectite, form a stack exhibiting the equivalence parameters of chondrodite ; superposing on this a second set of forsterite blocks leads to a stack showing the equivalence parameters of humite, and on again repeating the operation, a stack with the dimensions of clinohumite results. From the numerical data and the models exhibited it must be regarded as definitely proved that, in this series, the volumes appro-
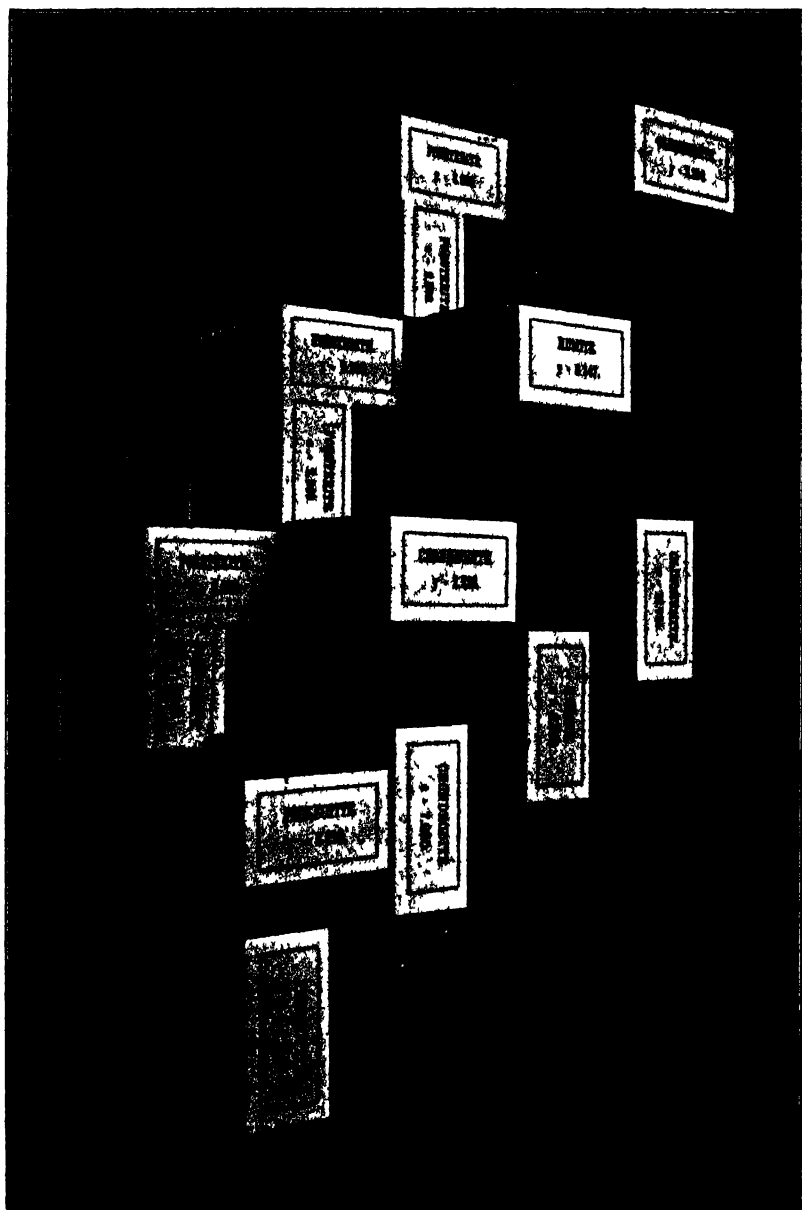
Fig. 5.

priated by the constituent atoms are, in any one member, directly proportional to the valency numbers of the corresponding elements.

Another set of observations of a very convincing character, although of a totally different kind, is laid out in Table IV.

TABLE IV.—MOLECULAR VOLUMES OF THE NORMAL PARAFFINS
AT THEIR MELTING POINTS.

—	W.	Melting Point t^o.	Molecular Volumes.	
			Observed at t^o.	Calculated as W × S.
$C_{11}H_{24}$	68	− 26·5	201·4	201·96
$C_{12}H_{26}$	74	− 12·0	219·9	219·78
$C_{13}H_{28}$	80	− 6·2	237·3	237·60
$C_{14}H_{30}$	86	+ 4·5	255·4	255·42
$C_{15}H_{32}$	92	+ 10·0	273·2	273·24
$C_{16}H_{34}$	98	+ 18·0	291 2	291·06
$C_{17}H_{36}$	104	+ 22·5	309·0	308·88
$C_{18}H_{38}$	110	+ 28·0	326·9	326·70
$C_{19}H_{40}$	116	+ 32·0	344·7	344·52
$C_{20}H_{42}$	122	+ 36·7	362·5	362 34
$C_{21}H_{44}$	128	+ 40·4	380·3	380·16
$C_{22}H_{46}$	134	+ 44 4	398·3	398·00
$C_{23}H_{48}$	140	+ 47·7	416·2	415·80
$C_{24}H_{50}$	146	+ 51 1	434·1	433·62
$C_{27}H_{56}$	164	+ 59·5	487·4	487·08
$C_{31}H_{64}$	188	+ 68·1	558·4	558·36
$C_{32}H_{66}$	194	+ 70·0	576·2	576·18
$C_{35}H_{72}$	212	+ 74·7	629·5	629·64

Mean value of S = 2·970.

Experimental determinations of the molecular volumes of a long series of normal paraffins, made on the liquid substances at temperatures at which the materials are in physically similar conditions, are stated in column 4. Since the valency of carbon is four times that of hydrogen it would be anticipated from the crystallographic conclusions previously drawn, that each carbon atom should appropriate four times as large a space for occupation as one hydrogen atom ; the quotient of the molecular volume by the valency sum or valency volume, W, should consequently lead to the same value, S, in the case of all the hydrocarbons. The mean value of S, namely, the atomic volume of hydrogen, is thus calculated as 2·970, and that it is constant within very narrow limits is seen on comparing columns 4 and 5, the latter of which states the product of the valency volume, W, by the value 2·970. The simple relation between the atomic volumes of carbon and hydrogen in the liquid normal paraffins indicated in the above table was recently pointed out by Lebas, and is

abundantly confirmed by numerous series of determinations in addition to that now quoted. It is thus definitely proved that the law of valency volumes, first enunciated on the ground of the crystallographic evidence, holds rigidly in the case of these liquid substances.

Sufficient has been said to demonstrate that a method has now been devised by means of which the vast stores of accurate goniometric measurements collected by crystallographers during the past century can be interpreted and that the requisite interpretation has in many cases already been given. Professor Liveing, in a discourse delivered in this room nineteen years ago, suggested that crystalline forms are the outcome of the accepted principles of mechanics ; the aid of these, and of these alone, has been invoked to show that crystalline structures result from the equilibrium of the attractive and repulsive forces radiating from the atomic centres.

[W. J. P.]

His Grace the Duke of Northumberland, K.G. D.C.L. F.R.S.,
President, in the Chair.

Professor Sir James Dewar, M.A. LL.D. D.Sc. F.R.S. *M.R.I.*,
Fullerian Professor of Chemistry.

Chemical and Physical Change at Low Temperatures.

The retarding effect of extremely low temperatures on chemical
action has long been known, and it was generally supposed that at a
sufficiently low temperature all such action would be completely
suspended. This inference was much shaken when it was found
that liquid hydrogen and solid fluorine combined with explosive
violence at 20 absolute.* One of the most characteristic reactions of
ozone is that it can be dissolved in carbon disulphide at a tempera-
ture of about –100 C., showing a deep blue colour, whereas on
slightly raising the temperature the colour disappears owing to rapid
oxidation. But perhaps the most remarkable of all low temperature
reactions is the fact mentioned in the Friday Evening Discourse, 1910,†
that solid oxygen at the temperature of boiling hydrogen is capable
of being partially transformed into ozone by the impact of ultra-violet
rays. In this case the action is clearly a molecular transition, involv-
ing the absorption of energy, taking place in the solid state in one
body, and not an interaction of two bodies as in the cases of ozone
and carbon disulphide, and the combination of liquid hydrogen and
solid fluorine.

Action of Ozone at the Temperature of Liquid Air.

A convenient method of illustrating the effects of low tempera-
tures on chemical action is by the use of liquid and gaseous ozone.
For the purpose of experiment its condensation can be easily effected
with the aid of liquid air, in the following manner. Oxygen, after
cleaning by passing through a U-tube B (Fig. 1) immersed in liquid
oxygen, is exposed to the silent electric discharge in the ozoniser C, and
bubbled through the tube D, the end of which dips into liquid air in

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* Moissan and Dewar, Comptes Rendus, vol. CXXXVI. p. 643.
† Proc. Roy. Inst., vol. XIX. p. 925.
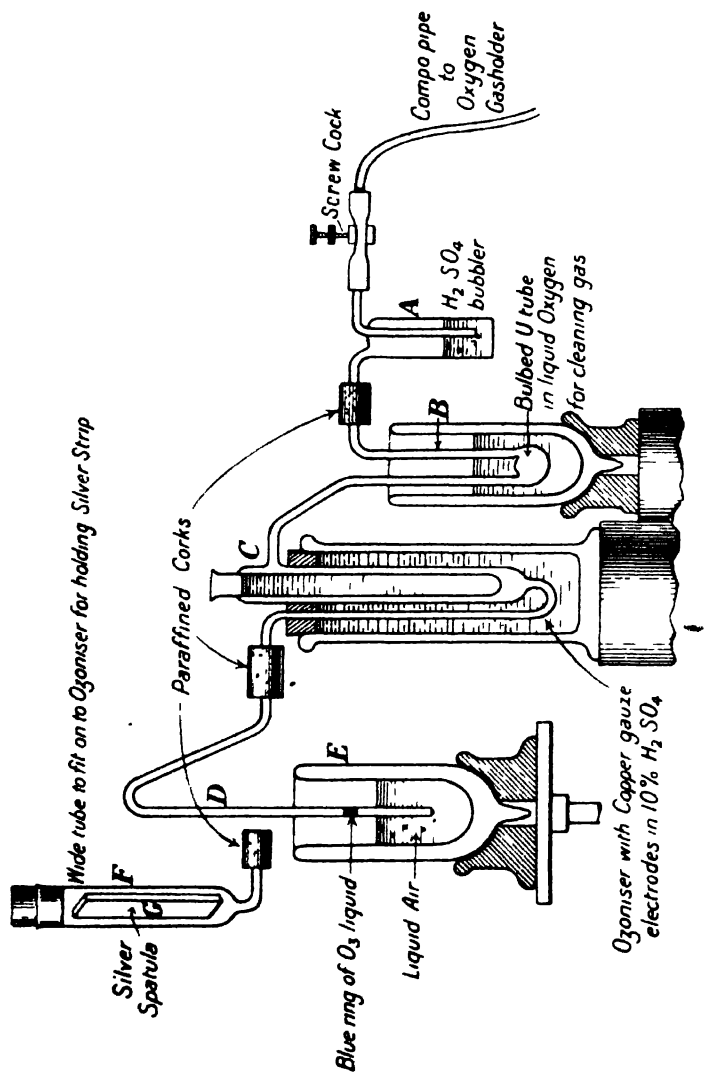
FIG. 1.

the vacuum vessel E.   In a short time a ring of blue liquid begins to form in the tube a little above the level of the liquid air.   This is condensed liquid ozone, which quickly dissolves when brought into contact with the liquid air.

The rapid oxidation of silver, as shown by the blackening of the metal which results from the action of ozone on a plate of polished silver at ordinary temperature, is well known ; if, however, a strip of silver G (Fig. 1) be cooled in liquid air and placed in the tube F connected to the ozoniser C and subjected to the action of the gaseous ozone, no blackening is noticed for a considerable time, but as soon as it warms up to the temperature of the room the strip turns black.   If a similar piece of silver be immersed in liquid air containing ozone in solution, and left there indefinitely, there is no apparent action and no blackening results.

From the early days of low temperature research it has been known that mere cooling to the temperature of liquid air does not destroy bacterial life, the organisms recovering their vital functions after weeks of immersion.   The bactericidal effect of the ultra-violet light was discussed in the Friday Evening Discourse, 1910, on Light Reactions at Low Temperatures,* when it was shown that the effect of the ultra-violet light on bacteria, even at the temperature of liquid air, was to pulverize the organisms.   It has been found by experiment that the bacteria can be protected from the action of the ultra-violet light by means of thin sheet lead.   Aluminium foil, on the other hand, is sufficiently transparent for the ultra-violet rays to remain effective in killing the bacteria.

Bacteria cooled in liquid air may also be subjected to the action of the cathode discharge in the following way.   A glass tube A (Fig. 2), provided with platinum electrodes B and C, is connected
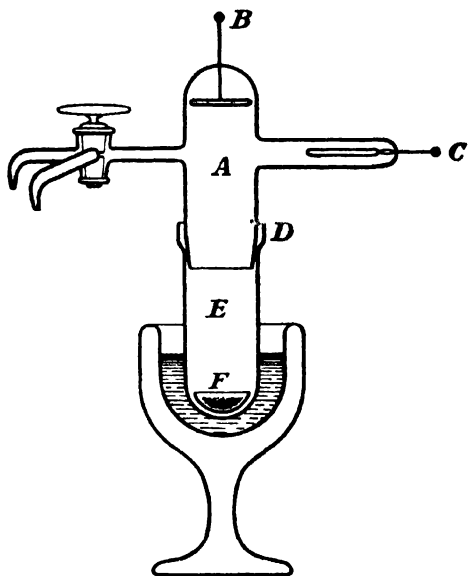
FIG. 2.

* Proc. Roy. Inst., vol. XIX., p. 921.

at D by means of a vaselined ground-glass joint to a tube E. The luminous bacteria, cultivated on a thin surface layer in a tin cup F, is placed in the bottom of the tube E, the end of which is immersed in liquid air. The united tubes are then sufficiently exhausted to allow the discharge to pass, and the cathode rays from B strike directly on the surface of the bacterial culture. Experiments have shown that hours of the cathode discharge will not kill the bacteria.

SOLIDIFICATION OF GASES.

With regard to the liquefaction and solidification of gases, all have been liquefied and solidified except helium, which still resists solidification, although its temperature has been reduced to below 3° abs.
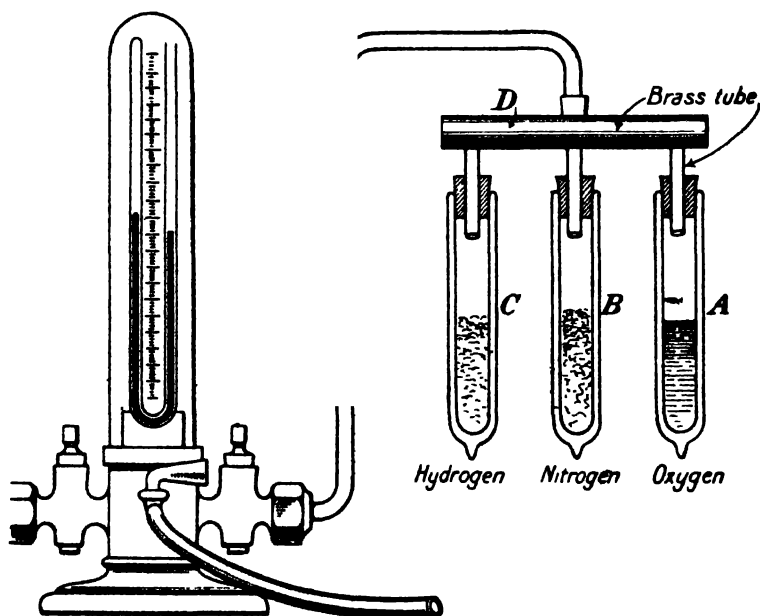
FIG. 3.

The solidification of oxygen has been finally accomplished by the aid of a charcoal vacuum and of thermal isolation, such as can be obtained with silvered vacuum vessels. The difference as regards solidification of the three liquids—nitrogen, hydrogen, and oxygen—

is plainly shown when they are made to boil by exhaustion in jacketed glass tubes (Fig. 3) connected to a powerful pump. The nitrogen and hydrogen turn into snowy solids; but the oxygen remains liquid.

It seems strange that while liquid hydrogen or nitrogen can be thus easily changed into the solid condition by evaporation under exhaustion, yet the ordinary air-pump fails to effect the transition of state in the case of liquid oxygen. This is due to the small vapour-pressure of solid oxygen at its melting point, as compared with hydrogen or nitrogen under similar conditions—together with the greater need of very perfect heat-isolation in the arrangement of the experiment. With the aid of charcoal as a gaseous condensing agent at low temperatures, combined with the employment of proper vacuum vessels, the change from the liquid into the solid can be effected. Pure liquid oxygen, contained in a properly isolated vessel, subjected to the exhaust produced by a quantity of charcoal kept at about the temperature of boiling oxygen, has its pressure lowered sufficiently to produce solidification to a transparent jelly. The pressure at which solidification takes place is determined by connecting a McLeod gauge to the vessel containing the solid oxygen.

About 75 grm. of good coconut charcoal is necessary to produce and maintain the necessary conditions of exhaustion. From 5 to 10 c.cm. of liquid oxygen are employed, previously exhausted by an air-pump. The oxygen exhibits considerable supercooling, and a pressure of less than half the melting pressure can usually be maintained on the liquid without producing solidification. These experiments indicate that the melting-point pressure is between 1·115 and 1·125 mm.

Fig. 4 shows the arrangement of the apparatus. Fig. 5 shows a modification, in which the oxygen is condensed in a bulb immersed in the solid oxygen produced by the charcoal exhaust.

In Fig. 4, A is a silvered vacuum-jacketed tube, with an uncoated slit, containing the oxygen to be exhausted. This is further isolated by a larger vacuum tube B, also silvered, and with a clear slit as above, which contains liquid air under an exhaust of less than 20 mm. A is sealed by the tube E on to a T-piece, whose limbs connect (1) through a constricted portion to bulbs containing permanganate of potash crystals and phosphoric anhydride respectively, (2) to a three-way cock C, to the arms of which are sealed (*a*) the bulb D, containing 75 grm. of coconut charcoal, (*b*) a T-piece connecting to the mercury-pump stopcock and the McLeod gauge. As soon as the charcoal vacuum is turned off the oxygen jelly melts, to solidify once more when the vacuum is again turned on. The reason of the peculiar behaviour of the oxygen will be understood from the following table, giving the melting-point pressures

Seal after condensing oxygen

*to P₂O₅ &
KMnO₄ bulbs*

to M°Cleod gauge

E

to exhaust

to

C

B

A

*to
Mercury
Pump*

D

Fig 4

to M°Cleod gauge

Seal after O filling

*to mercury pump
also vacuum tube
with liquid oxygen*

I

H

*to 3-way cock &
mercury pump & charcoal
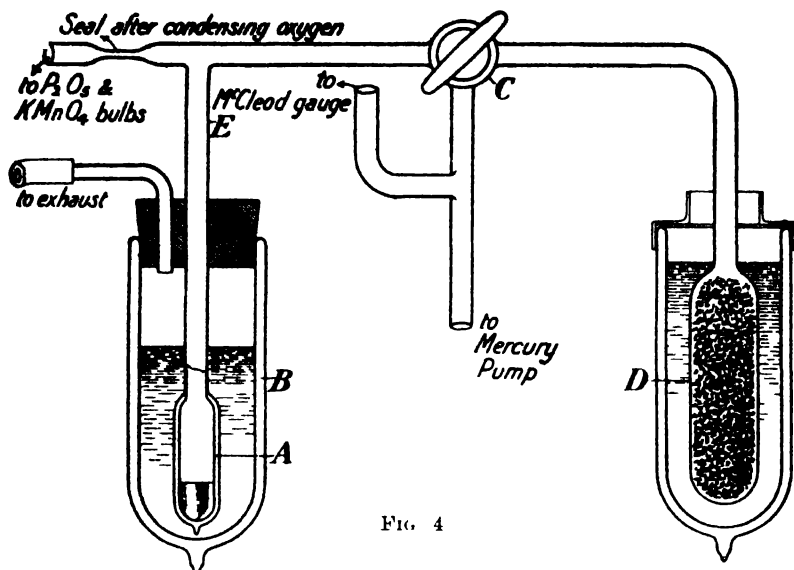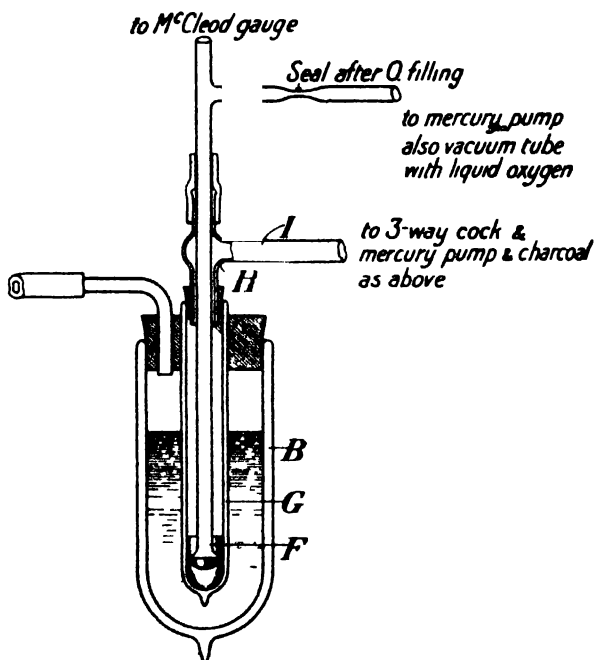as above*

B

G

F

Fig 5

(in millimetres of mercury), and the corresponding temperatures (in degrees absolute) for the chief gases :—

				Melting Point Pressure		Absolute Temperature
Helium	.	.	.	Below 2	mr	Below 2°·5
Neon .	.	.	.	350	,,	35°
Argon .	.	.	.	628	,,	85°
Krypton	.	.	.	158	,,	104°
Xenon .	.	.	.	86	,,	133°
Hydrogen	.	.	.	50	,,	14°
Nitrogen	.	.	.	90	,,	59°
Oxygen	.	.	.	0·9	,,	46°

Any good air-pump, capable of maintaining an exhaust below 0·1 mm. with a reasonable leak, can easily cause oxygen to solidify if thermally isolated.

SEPARATION OF MIXED GASES.

The easy application of low temperatures, combined with the use of charcoal, has led to a means of separating mixed gases by the use of various liquids as cooling agents. When the least volatile gas is condensed, the residual pressure is due to the more volatile gases, and finally to helium, which is the most difficult to condense.

The use of liquid hydrogen and charcoal as agents in the separation of gaseous mixtures may be shown as follows :—Two long glass tubes, A and B (Fig. 6), each originally full of ordinary air, are joined, B to a charcoal bulb dipped into liquid air, and A to a plain tube cooled in liquid hydrogen. Under the electric discharge, both tubes show the ruddy glow of mixtures of neon and helium. When the two cooling vessels are removed the discharge in A, cooled by liquid hydrogen, stops almost instantaneously ; the discharge in the other tube, B, cooled by liquid air and charcoal, continues almost unchanged for some time. The reason being that the cooling effect of the liquid hydrogen disappears almost instantaneously, while in the other tube the gases are only very slowly liberated from the charcoal after the cooling by liquid air is stopped.

In the following table the results of the separation of the rare gases in the atmosphere by different methods are given, the figures in the last column being those obtained by using liquid hydrogen as the cooling agent.

RARE GASES IN THE ATMOSPHERE.

Per Million Volumes.

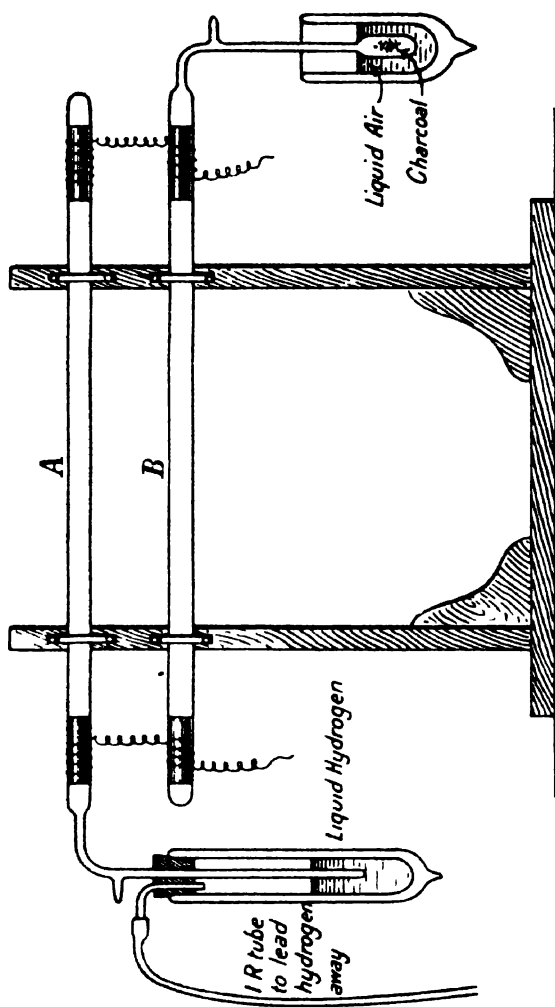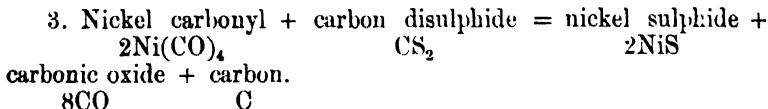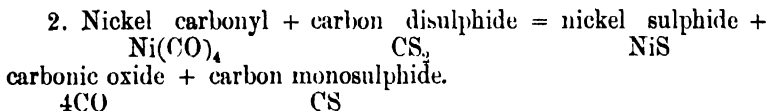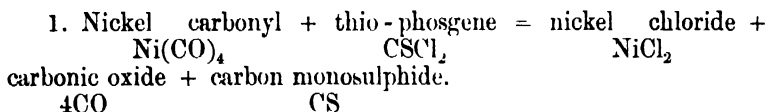|				1902 Dewar Float Method	1905 Ramsay Charcoal	1910 Claude Industrial Working	1910 Dewar Liquid Hydrogen
Total	.	.	.	17·2	16·4	20·0	20·0
Neon	.	.	.	14·4	12·3	15·0	15·0
Helium	.	.	.	2·7	4·0	5·0	5·0

FIG. 6.

THE PRODUCTION OF AN EXPLOSIVE GAS FROM CARBON DI-
SULPHIDE. SEPARATION BY CONDENSATION AT THE TEM-
PERATURE OF LIQUID AIR.

Such experiments suggest that there might be gaseous bodies
of so evanescent a character that their existence could only be
detected by their sudden condensation and freezing out at low tem-
peratures.   Carbon monoxide has a boiling-point of $-190°$ C., and
a melting-point of $-211°$ C., and is much more volatile than carbon
dioxide whose boiling-point is $-78°$ C., and melting-point $57°$ C.,
and a parallel relationship might be anticipated in the corresponding
sulphur compounds.   When studying the nickel carbonyls in con-
junction with the late Dr. H. O. Jones, such relationships seemed to
be reversed in the case of the carbon sulphides.   Pure carbon di-
sulphide is colourless, has a pleasant odour, and boils at $+40°$ C.,
while the monosulphide, separated by chemical means, was a brown
odourless powder.   By analogy, therefore, it might be inferred that the
boiling-point of the carbon monosulphide ought to be about $-180°$ C.

The reagents used to produce the monosulphide were thio-
phosgene and carbon disulphide acting on nickel carbonyl.   The
possible molecular reactions are three in number :

1. Nickel   carbonyl + thio - phosgene = nickel   chloride +
     $Ni(CO)_4$ $CSCl_2$ $NiCl_2$
carbonic oxide + carbon monosulphide.
   $4CO$ CS

2. Nickel   carbonyl + carbon   disulphide = nickel   sulphide +
     $Ni(CO)_4$ CS_2 NiS
carbonic oxide + carbon monosulphide.
   $4CO$ CS

3. Nickel   carbonyl + carbon   disulphide = nickel   sulphide +
     $2Ni(CO)_4$ CS_2 $2NiS$
carbonic oxide + carbon.
   $8CO$ C

When the densities of solid carbon disulphide, carbon dioxide,
and this chemically separated monosulphide were observed, the
following results were obtained : Carbon disulphide $[CS_2] = 52·4$;
Polymerized substance $(CS)_x = 24$; Carbonic acid $[CO_2] = 28·7$;
Carbon monoxide $[CO] = 28$.   It thus appears possible that the sup-
posed monosulphide is really $(CS)_x$, a polymerized body, and that the
real monosulphide might be isolated by means of the freezing-out
process.

ISOLATION OF THE MONOSULPHIDE.

With the object of attempting the isolation of such a substance
by the action of the " silent " electric discharge on carbon disulphide
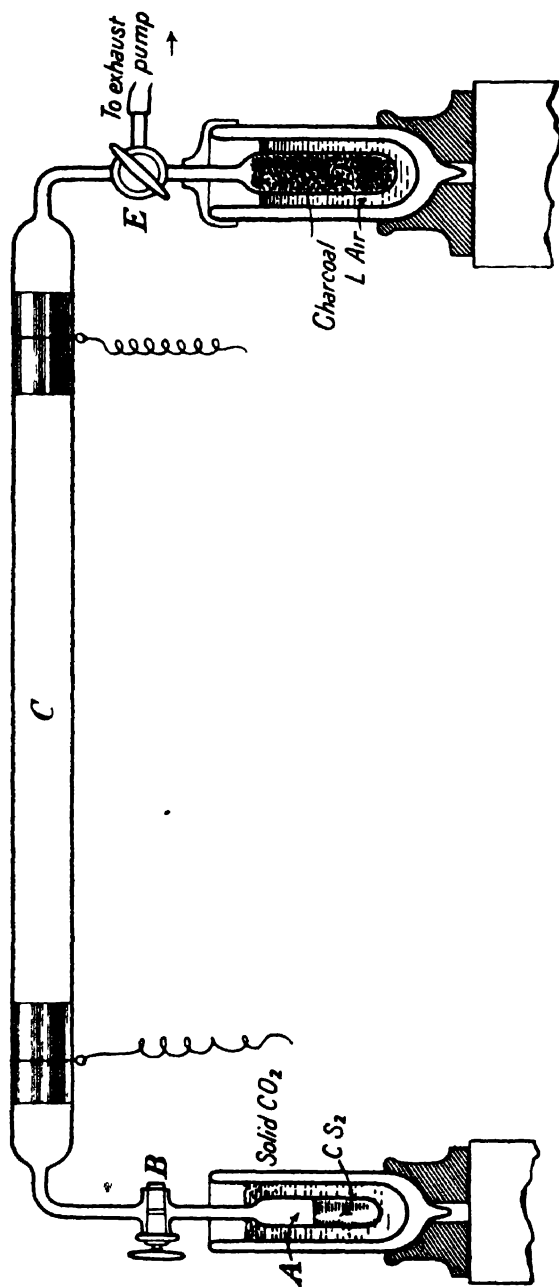
Fig 7.

vapour, the following apparatus (Fig. 7) was devised. A discharge tube C, 3 ft. long and 2 in. diam, provided with outside tinfoil electrodes, is highly exhausted by a charcoal bulb in liquid air, so that no electric discharge will pass. A small carbon disulphide reservoir cooled to $-80°$ C. in solid carbonic acid is also connected to the discharge tube through the stopcock. When this stopcock is momentarily turned on, the tube is charged with carbon disulphide vapour at about 1 mm. pressure, and the discharge is of a uniform lilac colour. This, however, rapidly diminishes in intensity, and in a few minutes ceases, showing that a high vacuum has been produced. The carbon disulphide is dissociated by the electric discharge into sulphur and carbon monosulphide, the latter rapidly polymerizing to a non-volatile form at the room temperature, as evinced by a brown stain produced on the interior surface of the tube.

Another method of detecting this monosulphide is shown in Fig. 8, where a litre bulb H containing carbon disulphide vapour that has been subjected to the electric discharge can be cooled locally by means of a pad of cotton wool saturated in liquid air, and thus any condensable material obtained as a deposit on the interior of the bulb. Before the discharge is turned on, the carbon disulphide distilling through the apparatus may be deposited by this local cooling as a white spot which volatilizes on warming, leaving no residuary mark. After the discharge is started the patch obtained in this way is yellow, changing quickly to dark brown on removal of the cooling pad, it does not volatilize on warming, but leaves a permanent brown film. The evanescent character of the body thus produced may be seen by stopping the discharge and leaving the tube for a few minutes fully charged with carbon disulphide vapour as it was before the local cooling. When the pad is again applied nothing but the white carbon disulphide can be condensed, and no brown film results.

The actual isolation of the volatile unstable monosulphide can be accomplished in the following way. The apparatus (Fig. 8), consists of a tube B containing carbon disulphide placed in a Dewar vessel filled with a paste of solid carbon dioxide and alcohol, communicating through a tap C with the annular space of the ozoniser A, the carbon disulphide thus giving off vapour at a pressure of $0·8$ mm. of mercury, which has proved most suitable for the passage of the electric discharge to effect decomposition of the disulphide into the monosulphide. The resulting gas is passed through an exhausted U-tube L, a few millimetres in diameter, placed in liquid air. A little above the level of the liquid air a brown ring condenses in the U-tube. This is the real monosulphide. When the liquid-air vessel is removed the tube explodes, and the fragments of glass are found to be partly covered with a brown powder consisting of the polymerized monosulphide. It would appear that
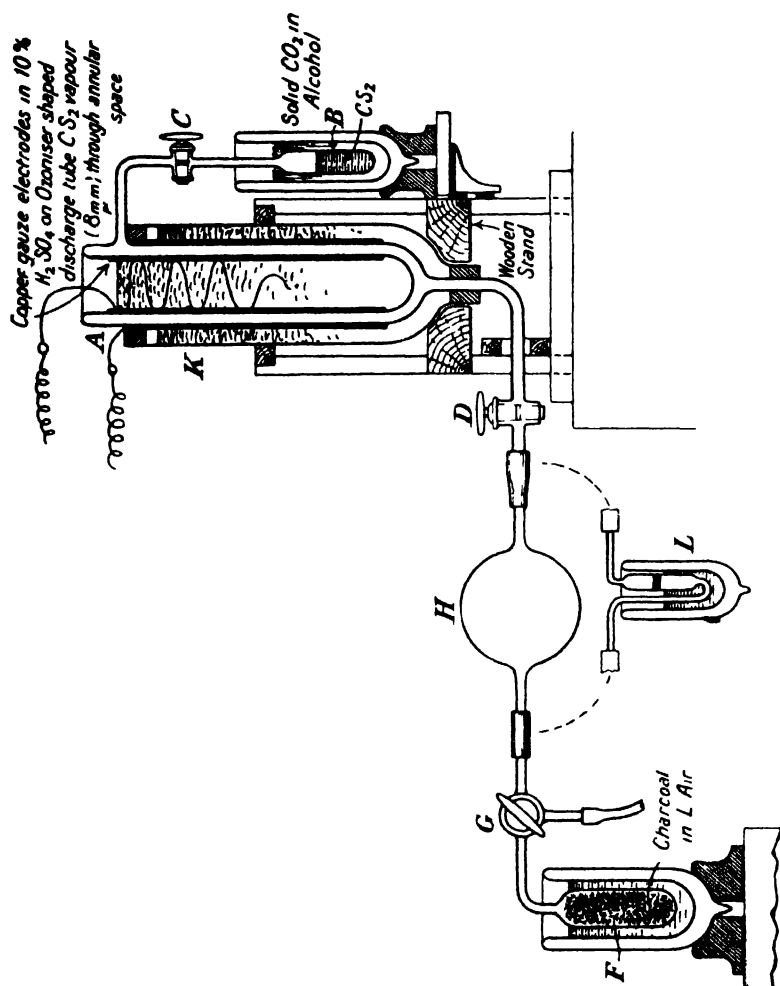
Copper gauze electrodes in 10% H_2SO_4 on Ozoniser shaped discharge tube CS_2 vapour (8mm) through annular space

Solid CO_2 in Alcohol

CS_2

Wooden Stand

Charcoal in L Air

Fig 9

this explosive polymerization takes place a little above the temperature of liquid air, and possibly also at a still lower temperature, though more slowly. At normal temperature the real monosulphide can only exist for about half a minute ; under ordinary circumstances it at once polymerizes, or its temporary existence, at any rate, cannot be detected.

A number of experiments made to ascertain if the phenomena were in any way dependent on the presence of impurities proved that when carbon disulphide, however purified, distilling from the liquid kept at $-78°$ C. into a charcoal condenser cooled to $-185°$ C. was submitted to the action of the silent electric discharge, and the vapour together with any new product condensed in a U-tube placed in liquid air, a brown solid resulted, the formation of which was accompanied by a glow or a flash and usually by a detonation on removing the liquid air surrounding the U-tube. Hence it is clear that these phenomena are not caused by the presence of impurities in the carbon disulphide, and that the evolution of light and heat are definitely associated with the transformation of the condensed gaseous product into the brown solid. It will be seen later that the flash and the detonation are to some extent variable phenomena.

The apparatus may be modified by connecting the ozoniser by means of a 3-way tap with two similar U-tubes packed with finely shredded cotton wool or asbestos offering an equal resistance to the passage of the stream of carbon disulphide vapour, and through a second 3-way tap to the charcoal condenser immersed in liquid air. When it was desired to observe the action of substances such as finely divided metals on the gases from the ozoniser these substances were either mixed with or deposited on asbestos, so that the deposit obtained when the gases were passed through it and subsequently condensed by liquid air could be compared with that obtained when the gases had passed over pure asbestos. Alternatively, either tube could be left free of any filtering material, and the character and proportion of the material deposited compared.

In order to ascertain if the rate of production of the brown solid could be increased, experiments were made in which the vapour of carbon disulphide evolved from the liquid at different temperatures between $-78°$ C. and $0°$ C. was allowed to pass through an apparatus in which an ordinary vacuum tube with flat platinum electrodes replaced the ozoniser, and from this entered the wide tube condenser which replaced the U-tube used in other cases. The surface of the vacuum tube soon becamec coated with a whitish deposit of sulphur, and later with the brown solid. The product condensed at the temperature of liquid air transformed into a brown solid with the evolution of light and heat as usual, and this also occurred when the vapour had passed through a cotton-wool filter.

Experiments were also made in which the ozoniser was either cooled to $-80°$ C. or heated to $220°$ C., the other conditions being as usual.

In both cases the brown solid was formed in the U-tube, but the quantity obtained was less than under the ordinary conditions of temperature.

In none of the experiments was the amount of brown solid obtained greater than in those in which the vapour from carbon disulphide at − 78° C. was passed through an ozoniser, and these conditions were therefore adopted for all subsequent experiments.

The determination of the ratio between the amounts of brown solid formed in the U-tube and of carbon disulphide passed through the ozoniser was found to be difficult owing to the almost invariable breaking of the tube during the transformation.

The ratio of the weight of the solid to that of the carbon disulphide varied from 1 to 10 to 1 to 50 in different experiments, and was found to depend on the form of the apparatus and the amount of solid surface over which the ozoniser product passed. Another very potent influence was found to be the deposit on the ozoniser surface. A clean ozoniser gave a much larger quantity of brown solid than an ozoniser that was coated with a deposit.

The Transformation of the Condensed Ozoniser Product into a Non-Volatile Solid.

The solid deposited in the condenser at − 185° C. is at first white, but soon acquires a brown colour, the darkest portion being nearest the liquid air surface. On allowing the temperature to rise, the brown colour spreads rapidly, and this change is usually accompanied by a glow or flash and a detonation which may be violent enough to shatter the condenser. The transformation may, however, take place quietly without an audible detonation or a visible flash, and, on the other hand, a detonation may take place while the condenser is still immersed in liquid air.

The interposition of a cotton-wool filter between the ozoniser and the condenser diminishes the intensity of the phenomena observed in the condenser to a very considerable extent, and at the same time increases the rate at which the brown solid is deposited in the ozoniser and leading tubes.

Quantitative experiment showed that the interposition of cotton-wool filters reduced the rate of flow of carbon disulphide to about one-fourth its former value, and the amount of brown solid to about one-fifteenth.

When the U-tube was replaced by a condenser of the test-tube form cooled to − 210° C. by immersion in liquid air under exhaustion and the gases admitted, the solid deposit which was formed on the bottom of the wide tube was perfectly white. After 15 minutes, however, the deposit had acquired a brown colour, showing that even at − 210° C. the transformation was taking place slowly. On allowing the temperature to rise to − 185° C. the transition took place more rapidly.

EXAMINATION FOR THE PRESENCE OF SOLID PARTICLES IN THE GASES FROM THE OZONISER.

A litre bulb with a U-tube on either side was sealed between the ozoniser and the charcoal condenser, and an arc lamp arranged to project a beam of light through this relatively large space filled with the transforming material from the ozoniser.   The glow in the ozoniser was screened off, and thus any solid particles in the bulb would be made evident by the illumination of the beam through the bulb.
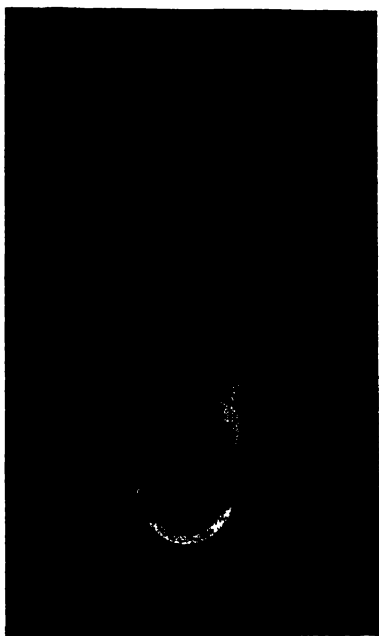
FIG. 9.

The arc lamp beam within the bulb was invisible, whether it was arranged converging to a focus or parallel.   Several good patches of transforming material were condensed on the bulb by local cooling with a cotton-wool plug soaked in liquid air; 35 seconds after turning off the discharge in the ozoniser only white carbon disulphide was thus condensed, all the transforming material having gone.   A five minutes' deposit in the second U-tube beyond the litre bulb gave the usual detonating trans-formation, and shattered the tube.   A similar deposit in the first U-tube produced, however, a distinctly more violent effect, and 2 or 3 inches of the tube were completely shattered.   No cotton-wool plug was used between the ozoniser and the bulb in the above experiment.

Similar results as to the non-visibility of the beam within the bulb were obtained when a cotton-wool plug was used ; but the deposits now gave less violent transformations.   These observations indicate that the transformation of the gas into the brown solid only takes place in contact with solid surfaces.

Theoretically, the detonation of carbon disulphide with the pro-duction of carbon and sulphur could produce a temperature above 2000° C., and if the transforming ozoniser product is comparatively endothermic, then a similar rise of temperature might occur if it could decompose in the same manner.

The high temperature produced during the transformation has been proved by taking a photograph of the U-tube by its own detonating flash (Fig. 9). The cracks in the fractured tube are plainly visible, a flame is seen bursting through one such crack, and the light extends for a considerable distance through the tube.

Before allowing the deposit to flash by the removal of the liquid air, in some experiments the U-tube was filled with dry nitrogen at atmospheric pressure, through a 3-way tap on the charcoal bulb. The right-hand limb of the U-tube contained copper wire gauze to cool the entering nitrogen and thereby prevent any undue heating of the deposit.

Two seven-minute deposits were successfully flashed after filling with nitrogen. In both cases a violent detonation resulted, and the tube was shattered. The photographic plates showed good pictures of each flash, which was seen to be localized and not so intense, due no doubt to the relatively large pressure of nitrogen in the U-tube compared with previous experiments in which no inert gas was present.

PHOTOGRAPHS OF THE SPECTRUM OF THE FLASH.

The arrangement used to secure a photograph of the spectrum of the flashes consisted of a German silver U-tube with a quartz window at the top of one limb. The flash occurring in the tube was projected through this window by means of a quartz prism, and reflected on to the slit of a Hilger quartz spectrograph.

About seven flashes from deposits of 15 minutes' periods were necessary to get a good image of the spectrum.

The sulphur bands, wave-lengths between 384 and 392, and the cyanogen line 3885 were present. The principal hydrocarbon bands were plainly visible, of which that at 436–443 was the strongest in the whole spectrum. A strong band at 635–655 and scattered bands from 248 to 362 were present also, and fainter bands from 540 to 605.

The solid product obtained after the flashes taken in the metal tube was found to be a mixture of carbon and sulphur due to the high temperature of the flash, as the character of the spectrum tends to show.

A number of tests for electric effect in the transformation of the condensed ozoniser product had negative results.

ATTEMPTS TO CONCENTRATE THE NEW GAS.

It was found that the gas was completely condensed in a U-tube at $-185°$ C., but that a similar U-tube, with a cotton-wool plug in the limb remote from the ozoniser, cooled to $-120°$ C. by immersion in solid carbon dioxide under reduced pressure, allowed some of the gas to pass through it and to be condensed in a second U-tube at $-185°$ C.

The resistance of the cotton-wool plugs was estimated by cooling the second U-tube in liquid air. In five minutes a deposit 15 to 20 mm. in length was formed.

The two U-tubes being thus at $-120°$ and $-185°$ C. respectively, the discharge was started in the ozoniser. At first no coloured deposit could be seen in the U-tube in liquid air, but later the deposit became coloured, and in 20 minutes a distinct brown ring was observed at a point 3 mm. above the liquid air surface.

Where the gases entered the first limb of the U-tube at $-120°$ C. a white crystalline deposit was observed ; this did not melt until the temperature had risen almost to $0°$ C., when it distilled back into the bulb containing carbon disulphide.

This indicates that the ozoniser product contains two substances, and shows that the substance which gives rise to the brown solid is not condensed by cooling to $-120°$ C., but passes on and is slowly transformed into the brown solid in the U-tube at $-185°$ C.

ACTION OF COCONUT CHARCOAL AND RUBBER.

The vapours were passed over coconut charcoal at $-185°$ C., and the results showed that the ozoniser product is thereby absorbed, destroyed, or caused to polymerize. The same result was obtained when the charcoal was cooled to $-78°$ C. or heated to $250°$ C.

The vapours were also passed over finely shredded rubber in order to absorb some of the carbon disulphide. The brown solid was formed as usual, but the amount of carbon disulphide deposited with it was distinctly less. It therefore appears that a partial separation of the transforming ozoniser product from the disulphide has been effected.

A complete separation of the two substances seems to be for the present out of the question on account of the rapidity with which the ozoniser product polymerizes in the solid state at low temperatures.

ANALYSIS OF THE SOLID PRODUCT.

A sufficient quantity of the brown solid was collected ($0·1127$ grm.) to allow of the estimation of sulphur in it,

which gave	$S = 71·8$ per cent.,
CS requires	$S = 72·7$ per cent.

Further, the ratio $C:S$ was determined in another specimen collected from a number of experiments in which the condenser had been cracked and shattered. This specimen was probably contami-

nated with minute fragments of glass and also contained moisture. The material gave on analysis :—

$S = 61\cdot0$ per cent., $C = 24\cdot6$ per cent., and ratio $C : S = 1 : 0\cdot854,$

or, allowing for the 5 per cent. of water present as impurity,

$$C : S = 1 : 0\cdot93.$$

The substance produced in the manner described has the composition of carbon monosulphide, and it seems justifiable to conclude that, under the influence of the silent electric discharge, carbon disulphide has, like carbon dioxide under similar conditions, been dissociated, in this case into sulphur and gaseous carbon monosulphide, and that the latter can polymerize with the evolution of a considerable amount of energy to form a brown solid even at the temperature of liquid air. It is the remarkable instability of the solid or liquid gas at low temperatures that is so characteristic and renders the physical and chemical examination so difficult.

CHEMICAL REACTIONS OF THE OZONISER PRODUCT.

The action of a number of substances on the ozoniser product was studied by placing the substances to be examined, either mixed with or deposited on asbestos in a U-tube, and allowing the vapours to pass over them.

In this way it was found that the passage of the ozonizer product was prevented by finely divided platinum, nickel, or silver.

Ferric oxide (not ignited), yellow mercuric oxide, and silver oxide were found to react with the ozoniser product to form sulphides of the metals ; ferric oxide is much more efficient than the other two.

Solid caustic potash, silver nitrate, lead acetate, and sodium peroxide seemed to have little or no action on the ozoniser product, while barium peroxide reacted with it, forming barium sulphide.

The most striking reaction observed is that which takes place with concentrated sulphuric acid. After some experiments had shown that, as used, the vapour of carbon disulphide was not attacked by sulphuric acid, the ozoniser product was allowed to pass over the surface of sulphuric acid placed in a wide U-tube. The sulphuric acid rapidly acquired a yellow colour, changing gradually into deep orange-red, then became turbid, and deposited a yellow solid ; brisk effervescence occurred during the whole time, and even after several hours none of the ozoniser product escaped the action of the acid. The yellow solid which separated from the sulphuric acid was found to be sulphur.

The properties of the brown solid produced from carbon disulphide which has the composition of carbon monosulphide, have been

compared with those of the polymeric form of carbon monosulphide obtained from the interaction of thiophosgene and nickel carbonyl, and the results indicate that the difference between the brown substance obtained by the action of the electric discharge on carbon disulphide vapour and the polymeric form of carbon monosulphide obtained from thiophosgene is merely in the degree of polymerization.

The Fullerian Professorship of Chemistry was endowed by John Fuller in 1833 as a recognition of the great work of Faraday. He held the office for thirty-four years, and if the lecturer is spared for a few months he will be able to look back on the same long period of service. Some member of the younger generation of chemists or physicists will soon have to continue the work of research at the Royal Institution.

[J. D.]

Friday, January 27, 1911.

Sir James Crichton Browne, M.D. LL.D. D.Sc. F.R.S.,
Treasurer and Vice-President, in the Chair.

Professor William H. Bragg, M.A. F.R.S.

Radioactivity as a Kinetic Theory of a Fourth State of Matter.

There are many points of resemblance between the movements of
the molecules of a gas and the movements of those corpuscular radia-
tions with which we have become acquainted in following up the
discovery of radioactivity. In both cases we find that things of ex-
tremely minute dimensions are darting to and fro with great velocity ;
and in both cases the path of any one individual is made up of straight
portions of various lengths, during which it is moving uniformly and
free from external influence, and of encounters of short duration with
other individuals, during which energy is exchanged and directions
of motion are altered. There is even a resemblance in the universality
of each movement. The motion of molecules is a fundamental fact
throughout the whole of our atmosphere, and indeed in all material
bodies ; the motion of the radiant particles emitted by radioactive
substances is also widely distributed, and of great importance. Taking
Eve's estimate of the usual ionisation of the air we can calculate that
in this room, in every second, some thousands of α and β particles
enter into existence, complete their paths through all the atoms they
meet, and sink into obscurity ; some of them, viz. the α particles, as
atoms of helium. Of these last some move through a range in air
of just over 4 cm., an equal number have a range of just under 5 cm.,
and again an equal number move through 7 cm. ; and the speed is so
great that the life of each α particle as such is completed in about a
thousand-millionth of a second. They leave their mark behind them
in the ionisation of the air through which they have passed, and in
the heat into which their energy has been commuted. The former
effect is easily detected by the sensitive measuring instruments which
we now possess ; the latter is too small to measure, and must be greatly
increased by the aid of radium itself before it can be investigated.
But on a large scale which takes into account the distribution of
radioactive material through the earth, the sea and the air, the effects
are of first rate importance to the physical conditions of our earth.

If we compare the movements a little more closely, we find differ-
ences as interesting as the resemblances. The motions which the
kinetic theory of gases considers are those of the molecules of which

gases consist : in the case of radioactivity, the things which move are quite different. They are sometimes electrons, which have come to be called β rays when their speed is great, and cathode rays when it is somewhat less ; or they are γ, or x rays, which are new things to us ; or if as a particles they are helium atoms, such as we have known before, they move with excessive speeds which give them quite new properties. In general the radiant particles move hundreds of thousands of times as fast as the gas molecules do, and it is, no doubt, on account of this fact, as well as through their usually extreme minuteness, that their power of penetrating matter is so great. When two molecules of a gas collide, they approach within a fairly definite distance, which we call the sum of the radii of the molecules : and the approach is followed by a recession and new conditions of motion. Each molecule has, as it were, a domain into which no other molecule can penetrate. But the defences which guard the domain are of no account to the vigorous movements which we are considering now. The radiant particles pass freely through the atoms, and their encounters are rather with one or other of a number of circumscribed and powerful centres of force which exist within the atomic domain, and act with great power when and only when approached within distances which are small in comparison with the atomic radius. It is on this account that the new theory opens out to us such possibilities of discovering the arrangement of the interior of the atom. Never before have we been able to pass anything *through* an atom : our spies have always been turned back from the frontier. Now we can at pleasure cause to pass through any atom an a particle, which is an atom of helium, or a β particle, which is an electron, or a γ, or x ray, and see what has happened to the particle when it emerges again : and from the treatment which it seems to have received we must try to find out what it met with inside.

The newer movement exists superimposed upon the other. Its velocities are so great that the gas (or liquid or solid) molecules are, in comparison, perfectly still. There is, as it were, a kinetic theory within a kinetic theory : there is a grosser movement of gas molecules which has long been studied, and in the same place and at the same time there is a far subtler and far more lively movement which is practically independent of the other. Your Vice-President, Sir William Crookes, was the first to find any trace of it. The behaviour of the cathode rays in the vacuum tubes which he had made showed him that he was dealing with things in no ordinary condition. Whatever was in motion was neither gas, nor solid, nor liquid, as ordinarily known, and he supposed it must be possible for matter to exist in a fourth state. We have gone far since Sir William's first experiments. The x ray tube and radium have widely increased our knowledge of phenomena parallel to those of the Crookes tube. But I think we may still be glad to use Sir William's definition.

There is another very striking characteristic of the newer kinetic

theory which differentiates it sharply from the older. The experiences of any one of the radiant particles in an atom which it crosses are quite unaffected by any chemical combination of that atom with others ; that is to say, by any molecular associations it may have. Naturally, this simplifies investigation. We may no doubt ascribe this state of things to the fact that a radiant particle is concerned rather with the interior of the atom than with the exterior, and that it is the latter which is of importance in chemical action.

Let us take notice of one more important difference. The molecules of a gas move with velocities which vary at every collision, yet vary about a certain mean. But the peculiar motion of the radiant particle is only temporary. For only a very short time can any ray be described as matter in a fourth state ; at the end of it the extraordinary condition has terminated, the particle has lost its tremendous speed or suffered some other change, and the ray ceases to exist. Speaking technically, we are dealing with initial not permanent conditions.

Let us now come back to resemblances between the two kinds of motion ; for there is one point of similarity which is not quite so obvious as others I have mentioned, and is, I think, of the greatest importance ; in fact, it is largely on account of this similarity that I have ventured to put the two theories together for comparison.

When the first experimenters in radioactivity allowed their streams of rays to fall upon materials of various kinds, they found that the irradiated surfaces were the sources of fresh streams of radiation. The secondary rays were sometimes of the same nature and quality as the primary, sometimes not. Further, they found that the secondaries, on striking material substances, could produce tertiaries, and so on. The examination of all the variations of this problem— the investigation of the consequences of changing the primary, of changing the substance, and last, but not least, of changing the form of the experimental arrangements—has been the cause of an enormous amount of work. There is a large literature dealing with secondary radiations of all kinds, which, I imagine, but few have read with any completeness, and the subject has become, on the surface at least, complicated and difficult. Now I believe that it is possible to clear away the greater portion of this complexity at a stroke, by the adoption of an idea which makes it possible to describe and discuss the whole of these phenomena in a very simple way. When an encounter takes place between two gas molecules, we suppose that the sum of the energies of the two is the same after the collision as before, and, further, that there are just two things to consider—two molecules— after as well as before. I think that we may carry this idea over almost bodily to the newer theory. A radiant particle encounters an atom. The particle is a definite thing, it contains a definite amount of energy, and whether it is an a or β or γ or x ray, its energy is to be found almost entirely inside a very minute volume. The

encounter takes place. When it is over there are still two things, an atom and a radiant particle going away from it. The sum of the energies of the two is still the same, which means that we deny a possibility much considered at one time—viz. that in the encounter the atom could be made radioactive, and could unlock a store of energy usually unavailable. We suppose there is no energy to be considered except the original energy of the radiant particle, and we suppose that there are not now two or more radiant particles in place of the original one, which also is a limitation on previous ideas. It is a theory which ascribes a corpuscular form to all the radiations. Each particle, a, β, γ or x, is to be followed from its origin to its disappearance, and we have nothing to think of but the one particle threading its way through the atoms. It loses energy as it goes, though little at any one collision, and it passes out of our reckoning when it has lost it all. There are no secondary radiations other than radiant particles moving in directions which are different from those in which they moved at first. Even when a cathode ray excites an x ray in the ordinary Röntgen tube, or the x ray excites a cathode ray in a manner almost as well known, it is hardly an exception to this rule. The cathode ray has an encounter with an atom and disappears ; simultaneously the x ray comes out of the atom, a circumscribed corpuscle carrying on the energy of the cathode ray. There is a change, but it extends only to the external characteristics of the carrier of energy. The x ray passes through the glass wall of the x ray bulb, or at least it does so sometimes ; it may pass through other matter as well, but sooner or later it has a fatal encounter with an atom, and the reverse change takes place. In all cases, in that of the undeviating a ray, or the β ray which suffers so many deflections, or the γ or x rays, it is a matter of tracing the movements of individual minute quantities of energy until they finally melt away.

Let us consider one or two simple experimental results from this point of view in order that we may illustrate this corpuscular theory, and at the same time may learn something of the properties of the corpuscles and of the arrangements of the atoms through which they pass.

We take first one of the simpler cases, the movement of an a particle through a gas. The relatively large mass of the particle gives it an effectiveness which the other radiations do not possess. It moves straight through every atom it meets, and ionises most of them. Very rarely does it suffer any deflection from its course until its velocity is nearly run down. Then indeed it does appear to depart considerably from the straight path, and it may be that it is much knocked about by collisions before it finally comes to comparative rest. In this way we may explain the distribution of the ionisation along its path, which increases slowly at first and rapidly afterwards, until the a particle has nearly finished its journey : it then falls off rapidly. Considering that the ionisation increases as the particle

slows down and spends more time in each atom, and considering the more broken nature of the path near its end, the reason of these peculiarities is clear enough. Apart from its comparative simplicity, there are some other very interesting features of the particle's motion. It is found, for example, that the loss of energy which the particle incurs in crossing an atom is proportional to the square root of the atomic weight very nearly, and there is no certain explanation as yet of this curious law. And again, Geiger has examined the small scattering that does occur, and found that a particles when moving quickly may be swung round completely even by the thinnest films of gold leaf, though the number is so small that the effect would have remained undetected had it not been for the scintillation method which he and Rutherford have perfected. He has found that about one particle in 8000 is returned in this way from a gold plate, which need consist only of a few thicknesses of gold leaf in order to give the maximum effect.

Now let us take an example from the behaviour of the β rays. The β particle is so light that it is easily deflected, even though it moves several times as fast as the heavier a particle. Because it therefore possesses little energy its effects are much smaller, and no one has yet succeeded in handling a single β particle in the same way as Rutherford and Geiger have handled the other. We are obliged to content ourselves with observations of the effects of a crowd of β particles, since the combined action of many is necessary to give us an observable result. And at the same time that the β particle gives much less effect than the a, it has a much more irregular course, so that the problem is doubly difficult. We are, in fact, only just beginning to understand it. There is a compensation in the fact that its very liability to deflection makes it all the more interesting an object. It is possible—and this is the particular β-ray problem I wish to consider now—to examine the deflection of a single β particle by a single atom : the parallel result in the kinetic theory of gases has never, of course, been achieved.

Suppose that we project a stream of β rays against a thin plate and measure the relative number sent back, which we do by measuring the ionisations caused by the incident and returned rays respectively. We do this for varying thicknesses of the plate, and plot the results, as, for example, Madsen has done. His plate was made of gold leaves, which could be had of extreme fineness. From the relation thus obtained, it is possible to obtain with confidence the amount of β radiation that would be returned by the thinnest plate that could be imagined, only one molecule thick. In such case the particles turned back could have had but one collision, and we have achieved our purpose. Madsen's figures show that a plate weighing 4 mmg. to the square centimetre turned back a tenth of the molecules that fell upon it, and as far as can be judged the ratio of the proportion turned back to the weight of the plate would be almost doubled for very thin

plates. We might go more into detail, and find the distribution of those that are returned ; we should then have data from which we might determine in some measure the distribution of the centres of force inside the atom. We cannot follow this up now, but I would like to draw your attention to a curious indication which we obtain when we compare the results for gold with those which Madsen found for aluminium. They show that the lighter metal turns back fewer β particles, and that its power of absorbing a stream of rays is rather an absolute abstraction of energy. There is clearly an actual absorption effect, which is to be distinguished from the scattering effect. Indeed, the two effects are obviously of different importance in the two cases. When a β ray strikes a gold atom it must be much more liable to deflection than when it strikes the lighter atom of aluminium. On the other hand, I think it can be shown clearly that in ploughing through aluminium atoms there is a relatively quicker absorption of energy. We may illustrate this by a rough model. Let us stand an electromagnet upright on the table, and let us suspend another magnet so that it can swing over the fixed one and just clear it. If we draw back the swinging magnet and let it go towards the fixed one, the currents running so that the two repel, then as the moving magnet tries to go by there will be a deflection depending on the relative speed, the closeness of approach, and the strength of the poles. This may represent the turning aside of an electron by a centre of force inside an atom. Now let the magnet at the table be supported by a spiral spring so as to be still upright, but have some freedom of motion ; then, when the experiment is repeated, the swinging magnet pushes the other more or less to one side ; it is less deflected, but it has to give up some of its energy. This is exactly what happens in the case of the β particle. The centre of force in the gold atom behaves like the stiffer electromagnet on the table ; it deflects the electron more, but robs it of less energy in doing so. It will not do to suppose the gold atom to differ from the aluminium atom simply in the number of centres of force, such as electrons, which it contains, if it is supposed that they all act independently. There is some other fundamental difference, equivalent to a difference in the stiffness with which the electrons are set in their places. There are two things to be expressed in the behaviour of the atom towards the β particle, as has been pointed out several times. H. W. Schmidt has actually calculated them from experiments which gave them indirectly and somewhat approximately. The method I have just outlined gives one of them directly, viz. that which is called the scattering coefficient ; and I think the other can also be found directly by a method which will serve as an illustration of the behaviour of γ rays.

We must first, however, consider the part which γ and x rays play generally in this theory. Workers are by no means agreed as to the proper way in which to regard them, but there is no need to

enter at once on a discussion as to their nature. It is well known that they have the most extraordinary powers of penetration, and are unaffected by electric or magnetic fields. They have one property which alone, as I think, brings them within our experience ; that is to say, the power of exciting β rays from the atoms over which they pass. Were it not for this, they would still be unknown. When we examine this production of β rays, we find that in the first place their speed depends on the quality of the γ rays which cause them, and not on the nature of the atoms in which they arise ; in the second, that the β rays to a large degree continue the line of motion of the γ rays as if the latter pushed them out of the atoms ; and, lastly, that the number of the β rays depends on the intensity of the γ rays. It is these facts which suggest the simple theory I have already described. The γ ray is some minute thing which moves along in a straight line without change of form or nature, which penetrates atoms with far greater ease than the a or β particle, which is not electrified, and which sooner or later disappears inside an atom, handing on a large share of its energy to a β particle which takes its place. The absorption of γ rays is simply the measure of their disappearance in giving rise to β rays, one γ ray producing one β ray, and no more.

We find the same sort of scattering in the case of γ rays as in that of β rays. Of a stream of rays directed against a plate which it can penetrate easily, we find that a few are turned completely back, a very much larger number are only slightly turned out of their path, and the rest go on. The scattered rays are very similar to the original rays : there is no need to suppose that the original ray disappears to be replaced by a secondary, any more than there is to suppose that a and β rays disappear and are replaced by others in similar cases. When therefore a γ ray enters an atom three possibilities await it. The first is a negative one, it may go through the atom untouched, and this must happen in the majority of cases ; the second chance is that of deflection, and the third that of conversion into a β ray, using the word conversion in a general sense without going into details as to the nature of the process.

Now we may consider our γ ray problem. Suppose a stream of these rays passing over a block of any substance such as aluminium or zinc or lead. When they are really penetrating rays they are equally absorbed by equal weights of these materials, which means that in equal weights equal numbers of β rays spring into existence. If these β rays were able to move through equal weights of the metals, we should find in each metal the same " density " of β rays ; and the important point is that this is independent of whether the rays are straight or crooked in their paths. If ten lines of given length were begun in every square centimetre of a sheet of paper, the ink used in drawing them would be independent of the straightness of the lines but proportional to their length. Now if we make a cavity in each

metal the β rays will cross it in their movements to and fro ; and if a little air is introduced into the cavity the ionisation produced in it will be a measure of the density of the β rays, and therefore the average distance each moves in the metal. Experiment shows that we get twice as much ionisation in a cavity in the lead as in a similar cavity in the aluminium, and we conclude that the β particle really has a longer track in the heavier metal. This experiment gives us the second constant of β ray absorption—that is to say, the rate at which its energy is taken away from it : the other experiment gave the chance of deflection only. We see that the path of a β ray in aluminium is more direct, but of less length, than in lead ; in the latter metal it has really a longer path, but it does not get so far away from its starting point because it suffers so many more deflections.

Finally, let us take a problem from the x rays. Let us see how we may test the idea that x and γ rays do not ionise themselves, but leave all the work to be done by the β rays which they produce. Suppose a pencil of x rays to pass across a vessel and to produce ionisation therein. It is convenient to use, not the original x rays, which are heterogeneous, but the rays which are scattered by a tin-plate on which the primary rays fall. Such " tin-rays," as we often call them briefly, are fairly homogeneous and give cathode-rays of convenient penetration. In some experiments of mine the rays crossed a layer of oxygen $3\cdot45$ cm. wide, having a density $\cdot00137$, and the ionisation produced was 227 on an arbitrary scale. The result may be put in the following way. Suppose, provisionally, that all this ionisation is done indirectly ; the oxygen has converted so much x-ray energy into cathode-ray energy, and these cathode-rays penetrating their one or two millimetres of oxygen, which is all they can do, have ionised the gas. Then we may say that in crossing a layer of oxygen weighing $3\cdot45 \times \cdot00137$, or $\cdot00473$ gr. per sq. cm., enough cathode-rays have been produced to cause an ionisation of 227 units : and therefore that a layer weighing one milligram per sq. cm. would produce 48 units in the same way. We now proceed to compare this production in oxygen with the similar effect in a metal such as silver. Stretching a silver foil across the chamber in the path of the rays we find that under the same intensity of rays the ionisation is largely increased, and the change is due to cathode-rays which the x-rays have generated in the silver. Not all these rays get out of the silver, but we can overcome this difficulty by taking silver foils of different thickness, drawing a curve connecting the effect of the foils with their thicknesses, taking the curve back to the origin, and so finding what would be the effect of a foil so thin that all the cathode-rays did get out. In my case I found that a milligram of silver produced enough cathode-rays to give an ionisation 1580. This is 33 times as much as the oxygen could do. Now according to our theory this should be because silver absorbs tin-rays 33 times more than oxygen does ;

and experiment showed this to be very nearly the case.   In finding the absorbing power of oxygen I measured first those of carbon and oxalic acid, and then proceeded by calculation ; for the absorption in a gas is difficult to determine.

Two interesting points appeared in this experiment.   In the first place the ratio between the two quantities of cathode rays, which appear on the two sides of a silver leaf through which the "tin rays" pass, is nearly constant for different thicknesses of leaf, and with the thinnest leaf obtainable each quantity was about half its full value. It would have been desirable to have had still thinner leaves ; but it is fairly clear that the ratio would be nearly the same for extreme thinness.   The cathode radiation, which appears on the side of the leaf whence the x rays emerge, is $1\cdot30$ times that which appears on the other, and we may take it that this would be the case even if the leaf were but one atom thick.   Thus when an x ray plunges into an atom in which its energy is converted into that of a cathode ray, the cathode ray may emerge at any point, but there is a 30 per cent. greater chance that it will more or less continue the line of motion of the x ray than that it will not.   In previous work on the conversion of γ ray into β ray energy, I have found that the β ray may practically be supposed to continue the line of motion of the γ ray, so that re is a great difference in behaviour of the two classes of ray in this respect.   It is remarkable that the scattering of the γ rays shows also a much greater dissymmetry than is found in the case of the x rays.   It looks as if the β rays that appear when γ or x rays impinge on atoms are related rather to the scattered than to the un-scattered primary rays.   Putting it somewhat crudely, no doubt, it might be said that when a γ or x ray is deflected in passing through an atom, it runs a risk of being converted into a β ray in the process, so that β rays are found distributed about the atom in rough pro-portions to the secondary γ or x rays.   In the case of γ rays this practically amounts to their all going straight on at first: in the case of x rays the distribution is more uniform.

Another interesting point arises in this way.   When the x rays from tin are allowed to pass into the ionisation chamber through increasing thicknesses of silver foil, the cathode rays grow at a rate which is not represented by the exponential curve usually assumed. The amount is for some time more nearly proportioned to the thick-ness of the foil.   A second foil adds its own effect without destroying much of the one on which it is laid.   This may easily be ascribed to the relation of the ionisation due to the β particle to the energy it has to spend.   The ionisation is nearly all at the end of the path, and the second layer does not absorb the rays made in the first because they are still at the beginning of their career.

These few experiments which I have described may serve to illustrate both the justice and the convenience of placing all these rays, a, β, γ, and x, in one class.   We are tempted to consider them

all as corpuscular radiations of some sort, and we then look upon our researches into their behaviour as attempts to understand the collisions of the various new corpuscles with the constituent centres of force in the atoms. But if we ascribe corpuscular properties to the γ and x rays, we are led far away from the original speculations as to their nature. Stokes supposed them to be spreading æther pulses, but in his theory the energy of the pulse spreads on ever-widening surfaces as the time passes, and is utterly insufficient to provide the energy of the β rays which the γ or x rays excite. Some sort of mechanism has to be devised by which the energy of the γ ray moves on without spreading, so that at the fateful moment it may be all handed over to the β ray, which carries it on. I had the hardihood myself to propose a theory of this kind. My idea was that the γ or x ray might be considered as an electron which had assumed a cloak of darkness in the form of sufficient positive electricity to neutralize its charge. Nor do I see any reason for abandoning this idea, for it is at least a good working hypothesis. It means, of course, that not only does the energy of the β ray come from the γ ray, but the β ray itself.

Many insist that my neutral corpuscle is too material, and that something more ethereal is wanted. For it appears that ultra-violet light possesses many of the properties of x and γ rays. It can excite electrons to motion, and sometimes the speed of the electron depends on the quality of the light and not on the nature of the material from which it springs. They propose, therefore, a quasi-corpuscular theory of light, γ and x rays being included. The immediate objection to this proposal is that it seems to throw away at once all the marvellous explanations of interference and diffraction which Young and Fresnel founded on a theory of spreading waves ; and I do not think anyone has yet made good this defect. The light corpuscle which is proposed is a perfectly new postulate. It is to move with the velocity of light, keeping a circumscribed and invariable form, to have energy and momentum, and to be capable of replacing and being replaced by an electron which possesses the same energy but moves at a slower rate ; and, of course, it has to do all that the old light-waves did. The whole situation is most remarkable and puzzling. We are working and waiting for some solution which, perhaps, will come in a moment unexpectedly. Meanwhile, we must just try to verify and extend our facts, and be content to piece together parts of the puzzle, since we cannot, as yet, manage the whole. My object to-night has been to show you how we may conveniently bind together a large number of the phenomena of radioactivity into an easily-grasped bundle, using a kinetic theory which has many points of resemblance to the older kinetic theory of gases.

[W. H. B.]

Mouvement Brownien et Grandeurs Moléculaires.

Nous observons chaque jour des liquides en équilibre, dont toutes
les parties nous semblent immobiles. Si nous y mettons un objet
plus dense, cet objet tombe, tout a fait verticalement s'il est sphérique.
Enfin, quand il est arrivé au fond du vase, nous savons bien qu'il ne
lui arrive pas de remonter spontanément.

Ce sont là des notions bien familieres, et pourtant elles ne sont
bonnes que pour les dimensions auxquelles nos organes sont accoutumés.
Il suffit en effet d'examiner au microscope de petites particules
placées dans de l'eau pour voir que chacune d'elles, au lieu de tomber
régulièrement, est animée d'un mouvement très vif et parfaitement
irrégulier. Elle va et vient, tournoie, monte, déscend, remonte
encore, sans tendre aucunement vers le repos. C'est le *mouvement
brownien*, ainsi nommé en souvenir d'un de vos compatriotes, le
botaniste *Brown*, qui le découvrit en 1827.

Cette découverte si remarquable attira peu l'attention. Les
physiciens qui entendaient parler de cette agitation la comparaient,
je pense, au mouvement des poussieres qu'on voit à l'œil nu se
déplacer dans un rayon de soleil, sous l'action des courants d'air qui
résultent de petites inégalités dans la pression ou la température.
Mais, en ce cas, des particules voisines se meuvent à peu près dans le
même sens et dessinent grossièrement la forme de ces courants d'air.
Vous allez voir, au contraire, qu'il y a indépendance complète des
mouvements browniens de deux particules, même quand elles s'appro-
chent à une distance inférieure à leur diamètre.

Je vais, en effet, essayer de vous montrer ce phénomène, un des
plus beaux que nous ait livrés le microscope, et dont nous allons
démontrer qu'il est l'image fidele des mouvements moléculaires, ou
mieux, *qu'il est déjà un mouvement moléculaire* (aussi bien que les
radiations infra-rouges sont déjà de la lumiere).

Vous apercevez en ce moment sur l'écran la cinématographie de
l'agitation que possèdent dans l'eau des grains ronds de gomme-gutte
(de diamètre un peu inférieur à 1 millième de millimètre). Cette

cinématographie a été faite par MM. Victor Henri et Comandon (film Pathé) et m'a été obligéamment prêtée par eux. J'aimerais mieux vous faire directement regarder l'émulsion que voici, en projetant sur un écran la vision animée qu'en donne le microscope, mais le grossissement nécessaire est si fort que cette projection serait trop peu lumineuse pour ce grand amphithéâtre.

Vous voyez qu'on ne peut saisir, en cette agitation profondément irrégulière, aucun courant d'ensemble entraînant en même temps plusieurs particules. Elle ne peut donc être due à des trépidations de la plaque qui porte la gouttelette observée, car ces trépidations, quand on en produit exprès, produisent précisément des courants d'ensemble, que l'on voit simplement se superposer à l'agitation irrégulière des grains. D'ailleurs, le mouvement brownien persiste sur un bâti bien fixe, la nuit, à la campagne, aussi nettement que le jour a la ville, sur une table sans cesse ébranlée par le passage de lourds véhicules (Gouy). De même il ne sert à rien de se donner beaucoup de peine pour assurer l'uniformité de température de la gouttelette. Tout ce qu'on gagne est encore seulement de supprimer des courants d'ensemble parfaitement reconnaissables et sans aucun rapport avec l'agitation irrégulière observée. On ne gagne rien non plus en diminuant extrèmement l'intensité de la lumière éclairante ou en changeant sa couleur (Gouy).

Bien entendu, le phénomène n'est pas particulier à l'eau, mais se retrouve dans tous les fluides, d'autant plus actif que ces fluides sont moins visqueux, et par suite il est surtout vif dans les gaz. Je vous montrais, il y a un instant, la cinématographie de grains de gomme gutte dans l'eau ; en voici une autre que je dois à l'obligéance de MM. Victor Henri et de Broglie, et qui vous montre le mouvement brownien dans l'air des gouttelettes ultra-microscopiques qui forment la fumée de tabac.

Dans un fluide donné, la grosseur des grains importe beaucoup, et l'agitation est d'autant plus vive que les grains sont plus petits. Cette propriété fut signalée par Brown, dès le premier instant de sa découverte. Quant à la nature des grains, elle paraît avoir peu d'influence, si elle en a. Dans un même fluide, deux grains s'agitent de même quand ils ont la même taille, quelle que soit leur substance et quelle que soit leur densité (Jevons, 1869). Et, incidemment, cette absence d'influence de la nature des grains élimine toute analogie avec les déplacements que subit un morceau de camphre jeté sur l'eau.

Enfin—et ceci est peut-être le caractère le plus étrange et le plus véritablement nouveau—le mouvement brownien ne s'arrête jamais. A l'intérieur d'une cellule close (de manière à éviter l'évaporation), on peut l'observer pendant des jours, des mois, des années. Il se manifeste dans des inclusions liquides enfermées dans le quartz depuis des milliers d'années. *Il est éternel et spontané.*

L'ensemble de tous ces caractères impose la conclusion que les

grains observés servent seulement a révéler une agitation propre au fluide lui-même, ce qu'ils font d'autant mieux qu'ils sont plus petits ; (c'est ainsi qu'un petit bateau suit plus facilement qu'un gros le mouvement des vagues de la mer). Nous atteignons par là une propriété essentielle de ce qu'on appelle un fluide en équilibre : ce repos apparent n'est qu'une illusion, due à l'imperfection de nos sens, et correspond en réalité à un certain régime permanent d'agitation violente et spontanée.

J'aurais voulu vous dire comment cette agitation perpétuelle, enlève au second principe de la thermodynamique le rang d'une véritete absolulue (Gouy, 1888), et le réduit à une loi de statistique, c'est à dire à l'affirmation de probabilités d'autant plus faibles qu'on les applique à des systèmes plus petits, mais le temps nous est trop mesuré, et je veux tout de suite chercher quelle cause intérieure au fluide peut expliquer le phénomene.

Nous devrons, pour deviner cette cause, faire appel aux hypothèses moléculaires. Vous savez combien elles sont anciennes, puisque déjà *Démocrite* et *Leucippe* pressentirent, il y a plus de vingt siecles, que la Matiere est faite de grains indestructibles en mouvement incessant, atomes que le Hasard, ou le Destin, aurait groupés au cours des âges, selon les formes et les corps qui nous sont familiers. Mais la tradition seule nous renseigne sur ces premieres théories, et, dans le beau poëme déjà très postérieur où Lucrece expose l'atomisme d'Epicure, je n'ai rien vu qui indique la façon dont les philosophes grecs ont été conduits à attribuer á la Matiere une structure granulaire.

Il me semble que cette hypothese a pu leur être suggérée par les propriétés si familieres des mélanges. En tout cas, il y a dans ces propriétés un argument déjà sérieux, que je veux donner d'abord. Nous disons tous, par exemple, après avoir dissous du sucre dans de l'eau, que le sucre et l'eau subsistent dans le mélange, bien qu'on ne puisse pas distinguer dans l'eau sucrée des parties différentes. De même nous disons qu'il y a de l'oxygene dans l'air et plus généralement nous *reconnaissons* souvent sans hésitation, au travers des propriétés d'un mélange, celles de ses constituants.

Cela se comprendrait facilement, si les corps qui ont formé le mélange y subsistaient comme subsistent à côté les uns des autres la fleur de soufre et la limaille de fer que je mélange sous vos yeux. Vous ne pouvez plus à présent distinguer les grains jaunes des grains noirs, et le tout a pris à vos yeux une coloration grise bien homogene. Vous y reconnaissez le fer, pourtant, même de loin, si j'approche un aimant du ballon qui contient le tout, et cela ne vous surprend pas, car vous savez bien qu'il vous suffirait de vous approcher pour distinguer les grains de fer et de soufre juxtaposés, mais non modifiés. De même, la persistance des propriétés du sucre dans l'eau sucrée s'expliquera tres bien si dans cette solution se trouvent simplement mêlées, juxtaposées, de petites particules qui à elles toutes seules,

formeraient de l'eau, et d'autres particules qui prises de même seules ensemble formeraient du sucre. Ces particules élémentaires, ces *molécules*, se retrouveraient dans tous les mélanges où l'on reconnaît de l'eau ou du sucre, et leur extrême petitesse nous empêcherait seule de les percevoir individuellement.

De plus, les molécules d'un corps pur comme l'eau, si elles existent, doivent être identiques, sans quoi elles ne réagiraient pas de même aux divers essais de fractionnement, à l'ébullition par exemple, et les fractions successivement séparées ne seraient pas identiques, alors qu'en fait elles le sont. (Dalton.)

Toujours si les molécules existent, nous sommes forcés, pour comprendre les dissolutions ou les diffusions, d'admettre qu'elles s'agitent sans cesse. Versons avec précaution de l'alcool sur de l'eau, ou superposons du gaz carbonique et de l'hydrogène (Berthollet) et abandonnons le système à température bien constante. Vous savez qu'alors les deux fluides se pénètrent progressivement, bien que le plus léger soit au-dessus, et cela ne se pourrait pas si leurs molécules restaient immobiles. Quand nous aurons ainsi vu que les molécules de gaz carbonique diffusent dans l'hydrogène, diffusent dans l'oxygène, diffusent dans l'azote, et ainsi de suite, il nous semblera bien probable qu'elles diffusent aussi dans le gaz carbonique lui-même, et cela revient à dire que les molécules du gaz carbonique sont en mouvement incessant.

Cette agitation des molécules explique aussitôt la pression qu'exercent les fluides sur les parois des récipients qui les enferment, pression qui sera due aux chocs des molécules contre ces parois. Cette explication, développée au dix-huitième siècle par Euler et Bernouilli, entraîne la loi de Boyle et permet de calculer la vitesse moyenne des molécules de divers gaz ; (dans l'air de cette salle, par exemple, les molécules auraient une vitesse moyenne d'environ 500 mètres par seconde). Ce résultat marque le premier succès, dans la Physique moderne, des vieilles hypothèses de l'atomisme grec.

Mais nous sommes encore loin d'une vérification directe, et les mouvements supposés des molécules nous échappent comme le mouvement des vagues de la mer échappe à un observateur trop éloigné. Cependant, si quelque bateau se trouve alors en vue, le même observateur pourra percevoir un balancement qui lui révèlera l'agitation qu'il ne soupçonnait pas. Ne peut-on de même espérer, si des particules microscopiques se trouvent dans un fluide, que ces particules, ces poussières encore assez grosses pour être suivies sous le microscope, soient déjà assez petites pour être notablement agitées par les chocs moléculaires ?

Vous devinez, maintenant, quelle explication nous allons donner au mouvement brownien. Tout granule situé dans un fluide est sans cesse heurté par les molécules voisines. Il n'y a aucune chance pour que ces chocs s'équilibrent exactement : notre granule sera donc irrégulièrement ballotté, et peut-être ce sera là le mouvement brownien.

Cette explication séduisante (Wiener, 1863), a été regardée longtemps comme douteuse. Pour qu'elle s'impose, il faut au moins que la théorie prévoie l'ordre de grandeur du phénomène, dont nous ne savons pas encore s'il n'est pas colossalement plus grand (ou plus petit) que ne le permet notre hypothèse.

Nous allons voir que cette vérification quantitative est possible, mais, pour y arriver, je dois vous rappeler d'abord comment, depuis longtemps déjà, la mesure des viscosités des gaz avait permis de trouver des valeurs probables pour la grandeur et le poids des molécules. Je vous montrerai ensuite que le mouvement brownien, supposé dû aux chocs moléculaires, donne également un moyen d'atteindre ces mêmes grandeurs moléculaires. Si les deux résultats obtenus par des chemins si différents concordent, l'origine du mouvement brownien ne sera plus douteuse.

Si l'on admet l'existence des molécules, on est conduit, pour expliquer les lois de discontinuité de la Chimie (loi des proportions définies, loi des proportions multiplés, loi des nombres proportionnels), à admettre avec votre illustre Dalton l'existence d'*atomes* caractéristiques des divers corps simples. Dès lors, en effet, la composition d'une molécule varie nécessairement par bonds discontinus, correspondant à l'entrée (ou à la sortie) de au moins 1 atome. Après quoi, on peut tirer avec précision, des phénomènes de *substitution* chimique, non pas les poids absolus des molécules et des atomes, mais les rapports de ces poids.

Quand par exemple on dissout du calcium dans l'eau, on chasse la moitie seulement de l'hydrogène de cette eau. Cela peut se comprendre si l'on admet que l'hydrogene de chaque molécule de cette eau se compose de deux parties égales. Il faut considérer ces parties comme insécables par tout moyen chimique puisque jamais une autre substitution ne conduit à en supposer plus de deux ; on dira que ce sont des " atomes " d'hydrogène. D'autre part, une molécule d'eau, comme toute masse d'eau, pèse 9 fois autant que l'hydrogene qu'elle contient ; elle pèse donc 18 fois autant qu'un seul atome d'hydrogène. On trouverait par une marche semblable que par exemple une molécule de benzine doit peser 78 fois autant que 1 atome d'hydrogene. Les poids des molécules de benzine et d'eau et de l'atome d'hydrogène sont donc entre eux comme 78, 18, et 1. On trouverait de même, en un grand nombre de cas, les rapports des poids de diverses molécules et de divers atomes.* Il est bien remarquable que toutes ces déterminations sont concordantes, en sorte que par exemple il faudrait compter par milliers le nombre des corps dont

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* A vrai dire tous ces rapports ne seraient pas encore atteints : par exemple, il n'est pas de substitution qui puisse renseigner sur le poids moléculaire d'un corps simple comme l'oxygène. Nous verrons dans un instant comment la loi d'Avogadro permet de combler cette lacune.

l'étude conduirait à dire que l'atome de carbone est 12 fois plus lourd que l'atome d'hydrogène. Cela donne confiance dans la théorie atomique, mais ne nous apprend absolument rien sur l'échelle des grandeurs moléculaires, peut-être proches de nous, peut-être infiniment lointaines.

On voit du moins que, pour avoir les poids absolus des divers atomes ou molécules, il suffirait de connaître l'un d'eux. Du même coup nous aurions aussi, comme l'a remarqué Helmholtz, la charge élémentaire que transporte dans l'électrolyse 1 atome d'hydrogene (et plus généralement 1 ion monovalent) Si en effet nous savions ce que pèse 1 atome d'hydrogene, nous saurions combien 1 gramme d'hydrogene contient de ces atomes, et par suite combien chacun transporte dans l'électrolyse, puisque nous savons que 1 gramme d'hydrogene y transporte environ 100,000 coulombs.

Tâchons donc d'atteindre l'un de ces poids élémentaires, celui de la molécule d'oxygene par exemple.

Théorie Cinétique.—Supposons qu'on liquéfie la masse d'oxygene qui occupe 1 litre (pression et température ordinaires) Les *n* molécules qui s'y trouvent vont venir presqu'au contact, car notre liquide est presque incompressible. Or, on sait que le volume vrai des grains d'un tas de sable vaut à peu pres les $\frac{2}{3}$ du volume apparent du tas ; il est donc probable que le volume vrai de nos *n* molécules n'est pas très inférieur aux $\frac{2}{3}$ du volume du liquide, et, en acceptant cette valeur on ne ferait déjà pas une erreur énorme. Une théorie plus precise, due à Van der Waals, conduit à admettre plutôt une valeur deux fois plus petite, et à écrire :

$$n \times \text{volume de 1 molécule} = \tfrac{1}{3} \text{ volume du liquide.}$$

D'autre part, à l'état gazeux, dans un volume donné, des molécules en nombre fixé *n* se heurtent d'autant plus souvent qu'elles sont plus grosses. Ou, si vous préférez, le libre parcours moléculaire moyen L est d'autant plus petit que les molécules sont plus grosses, ont plus de surface. Clausius et Maxwell ont pu calculer cette relation (en admettant les molécules sphériques) et ont trouvé :

$$n \times \text{surface de 1 molécule} = 0.7 \, \frac{\text{volume du gaz}}{\text{libre parcours moyen}}.$$

Si nous connaissions le libre parcours moyen, nous aurions donc, divisant ces deux équations l'une par l'autre, le rapport du volume $\frac{4}{3} \pi R^3$ à la surface $4 \pi R^2$, c'est à dire le rayon de la molécule, et par suite son volume et sa surface. L'une des deux équations, la première par exemple, nous donnerait alors *n*, nombre de molécules qui forment une masse connue d'oxygène. La masse de la molécule d'oxygene serait donc obtenue.

Mais il faut pour cela connaitre le libre parcours moléculaire.

Maxwell a su le déduire de la force qui s'exerce par frottement entre deux couches gazeuses qui glissent l'une sur l'autre avec des vitesses différentes.

Il est facile de montrer l'existence de ce "frottement intérieur," de cette "viscosité." Vous voyez le jet de gaz que j'allume au bout de ce long tube capillaire. Si maintenant je raccourcis le tube (en le coupant), le jet de gaz qui en sort donne une flamme beaucoup plus longue. Le gaz sort donc plus vite par un tube pourtant de même section. Il y avait donc un grand frottement dans la partie que j'ai supprimée, à l'intérieur de laquelle glissaient les unes dans les autres des gaînes gazeuses cylindriques.

L' hypothèse moléculaire explique aisément ce frottement. Pour le comprendre, imaginons deux trains de voyageurs se mouvant sur des rails parallèles avec des vitesses presque égales. Les voyageurs pourraient s'amuser à sauter sans cesse de l'un à l'autre, recevant chaque fois un léger choc. Grâce à ces chocs, les voyageurs tombant sur le train le moins rapide en accroîtraient lentement la vitesse, tandis que, de même, celle du train le plus rapide diminuerait lentement. Les deux vitesses s'égaliseraient donc, comme par un frottement, si on ne maintenait leur différence constante. Il en sera ainsi pour deux couches gazeuses qui glissent l'une sur l'autre, puis qu'elles se bombardent sans cesse, en s'envoyant l'une à l'autre des molécules.

L'analyse mathématique de cette idée si simple, faite par votre compatriote Maxwell, a montré que la force de frottement par centimètre carré entre deux couches gazeuses distantes de 1 centimètre et ayant une vitesse relative de 1 centimètre par seconde (force qui vérifie la viscosité) vérifie à peu près l'équation :

viscosité $= \frac{1}{3}$ densité $\times$ libre parcours $\times$ vitesse moléculaire.

La densité du gaz et la viscosité sont mesurables. Nous aurons donc le libre parcours si nous pouvons determiner la vitesse moléculaire (moyenne).

Ce dernier effort est facile. La pression du gaz, nous l'avons déjà dit, s'explique par les chocs incessants des molécules sur les parois, et ces chocs sont d'autant plus efficaces que chacune d'elles est plus lourde et plus rapide. Le calcul précis, dû à Bernoulli, donne :

pression $= \frac{1}{3}$ densité $\times$ carré de la vitesse moléculaire.

Ce qui détermine la vitesse cherchée. Appliquant à l'oxygène, ou trouve environ 500 mètres par seconde à la température ordinaire : les molécules que nous respirons sont aussi rapides que des balles de fusil.

Nous n'avons plus alors qu' à remonter de proche en proche : nous aurons le libre parcours moyen (1 dix-millième de millimètre pour l'air, dans les conditions ordinaires), puis le diamètre moléculaire

(une molécule d'oxygène est à un homme à peu près comme un homme est au soleil), puis le nombre n de molécules par litre (environ 30 milliards de trillions), puis enfin le poids de la molécule d'oxygène qui nous donnera, nous l'avons vu, tous les autres poids de molécules ou d'atomes.

On trouve ainsi, l'erreur possible étant largement de 30 %, que le poids de l'atome d'hydrogène vaut seulement le trillionième du trillionième de $1^{gr}6$, soit :

$$\frac{1^{gr}6}{1.000.000.000.000.000.000.000.000}$$

ou, plus brièvement, $1^{gr}6 . 10^{-24}$. Quant à la charge élémentaire, elle serait environ $5 . 10^{-10}$, soit environ le milliardième de la charge que peut déceler un électroscope ordinaire.

Je vais maintenant vous dire comment j'ai pu, grâce au mouvement brownien, donner d'autres moyens pour obtenir ces grandeurs moléculaires.

La loi d'Avogadro.—Je vous indiquais tout à l'heure comment l'étude des substitutions chimiques donne par exemple le rapport des masses des molécules de benzine et d'eau, qui doivent être entre elles comme 78 et 18. Deux masses de benzine et d'eau qui sont l'une à l'autre comme 78 est à 18 contiennent donc autant de molécules l'une que l'autre. Or, si nous mesurons les volumes occupés à l'état gazeux, par ces deux masses, à la même température et à la même pression, nous trouvons que ces volumes sont égaux. Ce n'est pas là un hasard, et de façon tout à fait constante on trouve que deux masses gazeuses qui doivent contenir autant de molécules occupent le même volume quand elles ont la même température et la même pression. C'est la loi d'Avogadro, que l'on peut énoncer comme ceci :

*Dans l'état gazeux, des nombres égaux de molécules de substances différentes, enfermées dans des volumes égaux à la même température, y produisent des pressions égales.**

Vous savez par ailleurs (loi de Boyle), que la pression ainsi développée varie en raison inverse du volume occupé.

Ces lois des gaz ont été étendues par Van 't Hoff aux solutions diluées. Il faut, bien entendu, considérer alors, non la pression totale exercée sur les parois, mais seulement la part de cette pression qui est due aux chocs des molécules dissoutes, portion appelée pression osmotique du corps dissous (et que l'on ne peut mesurer que si l'on sait réaliser une paroi " semi-perméable " qui arrête les molécules du

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* La loi d'Avogadro, une fois bien établie, nous donnera par extrapolation des poids moléculaires non atteints par la méthode des substitutions chimiques. Par exemple, quand nous aurons trouvé que 32 parties d'oxgène ou 2 parties d'hydrogène exercent dans le même volume (et à la même température), la même pression que 18 parties de vapeur d'eau, nous saurons que les masses de ces trois sortes de molécules sont entre elles comme 32, 2, et 18.

corps dissous, mais non pas celles du dissolvant).   Les lois d'Avogadro et de Boyle deviennent alors :

Dans l'état dilué (gazeux ou dissous), des nombres égaux de molécules quelconques, enfermées dans des volumes égaux à la même température y produisent la même pression.   Cette pression varie en raison inverse du volume occupé.

Ces lois sont indifféremment applicables à toutes les molécules, grosses ou petites.   Les lourdes molécules de sucre ou de sulfate de quinine ne comptent ni plus ni moins que la molécule d'hydrogène. Pourtant la molécule de sucre contient déjà 45 atomes, celle de sulfate de quinine en contient plus de 100, et l'on en trouverait aisément de plus complexes qui obéissent aux lois de Van 't Hoff (ou aux lois de Raoult, qui en sont la conséquence).

N'est-il pas alors supposable qu'il n'y ait aucune limite de grosseur pour l'assemblage d'atomes qui vérifie ces lois ; n'est-il pas supposable que même des POUSSIÈRES *déjà visibles les vérifient encore exactement, en sorte qu'un granule agité par le mouvement brownien ne compte ni plus ni moins qu'une molécule d'hydrogène en ce qui regarde l'action de ses chocs sur une paroi qui l'arrête ?   Ou, plus brièvement, est-il déraisonnable de penser que les lois des gaz parfaits s'appliquent encore aux* EMULSIONS *faites de grains visibles ?*

J'ai fait ce postulat, et c'est dans ce sens que j'ai cherché une expérience cruciale qui décidât de l'origine du mouvement brownien, et du même coup donnât ou retirât une base expérimentale aux théories moléculaires.

Voici celle qui m'a paru le plus simple :

La Repartition d'Equilibre, dans une Colonne Verticale de Matière Diluée.—Vous savez que l'air est plus raréfié sur les montagnes qu'au niveau de la mer, et que, de façon générale, une colonne de gaz s'écrase sous son propre poids, l'état d'équilibre résultant d'un antagonisme entre la pesanteur, qui fait tomber les molécules, et leur agitation, qui les éparpille sans cesse.

La loi de raréfaction, indiquée par Laplace (pour montrer comment l'altitude peut être donnée par le baromètre), est une conséquence nécessaire de la loi de Boyle, et peut s'énoncer de la manière suivante :

Chaque fois qu'on s'élève d'une même hauteur, la densité se trouve divisée par un même nombre.   Ou, plus brièvement : des bonds verticaux égaux s'accompagnent de raréfactions égales.

Par exemple, dans de l'air à la température ordinaire, la densité diminue de moitié chaque fois qu'on s'élève de 6 kilomètres (à partir de n'importe quel niveau).

Mais l'élévation qui entraîne une raréfaction double ne serait pas la même dans de l'hydrogène.   Un raisonnement simple montre que la façon dont influe la nature du gaz est une conséquence nécessaire de la loi d'Avogadro et peut s'énoncer comme ceci :

Les élévations qui entraînent une même raréfaction, pour deux gaz

différents (à la même température) sont dans le rapport inverse des poids des molécules de ces deux gaz.

Par exemple, si dans de l'oxygène à 0° il faut s'élever de 5 kilomètres pour que la densité devienne 2 fois plus faible, il faudrait s'élever de 80 kilomètres dans de l'hydrogène à 0° parce que la molécule d'hydrogène est 16 fois plus légère que la molécule d'oxygène.

Vous voyez ici (Fig. 1), un diagramme représentant trois éprouvettes verticales gigantesques (la plus grande a 300 kilomètres de haut), où
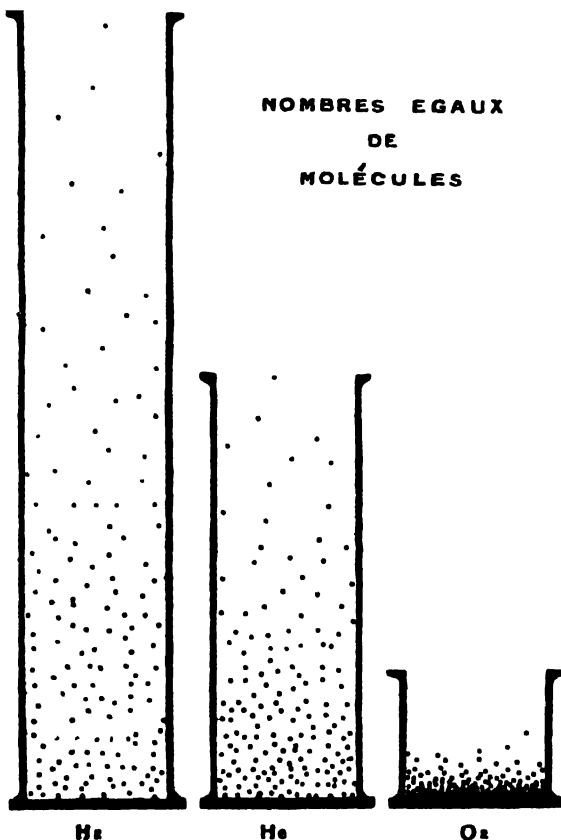

NOMBRES EGAUX
DE
MOLÉCULES

H₂   He   O₂

Fig 1.

l'on aurait mis en même nombre, des molécules d'hydrogène, des molécules d'hélium, et des molécules d'oxygène. A température supposée uniforme, les molécules se répartiraient comme l'indique le diagramme, d'autant plus remassées vers le bas qu'elles sont plus pesantes.

Or, nous avons été conduits à penser que les lois des gaz parfaits s'appliquent peut-être aux émulsions. Si cela est vrai, et si nous réalisons une émulsion où les grains soient égaux, la distribution de la matière dans une colonne verticale de cette émulsion devra être la même que pour un gaz. En d'autres termes, une fois atteinte la distribution d'équilibre, des élévations égales s'accompagneront de raréfactions égales. Mais s'il faut s'élever seulement de $\frac{1}{20}$ de milli-mètre, c'est à dire 100 millions de fois moins que dans de l'oxygène, pour que la concentration devienne 2 fois plus faible, on devra penser que chaque grain de l'émulsion pèse 100 millions de fois plus que 1 molécule d'oxygène. On aura donc ce dernier poids si on arrive à peser le grain, qui jouera le rôle d'un relai entre les dimensions moléculaires et celles qui sont a notre échelle.

Il est bien entendu que le poids efficace du grain sera la différence entre son poids réel et la poussée qu'il subit dans le liquide (con-formément au principe d'Archimède). Si les grains étaient plus légers que le liquide intergranulaire, c'est dans les couches supérieures qu'ils s'accumuleraient (des abaissements égaux entraînant des raré-factions égales). Ils se répartiraient uniformément s'ils avaient la même densité que le liquide.

Réalisation Pratique.—J'ai utilisé, pour réaliser ces expériences, les émulsions que l'on obtient en précipitant par l'eau les solutions alcooliques des résines. On obtient ainsi (comme vous le voyez), pour la *gomme-gutte* un beau liquide jaune, pour le *mastic* un liquide blanc comme du lait. Le microscope révèle dans ces liquides la résine précipitée sous forme de grains ronds *solides*, qui ne s'agglutin-ent pas quand les hasards du mouvement brownien les amènent au contact (ce qui arrive pour d'autre résines, qui donnent des grains mous).

Mais les diamètres de ces grains sont très variés et il me fallait les trier dè façon a réaliser des émulsions où tous les grains fussent à peu près de la même taille. Le procédé que j'ai employé peut se comparer au fractionnement d'un mélange liquide par distillation. De même que, pendant la distillation, les parties d'abord vaporisées sont relativement plus riches en constituants volatils, de même pendant la centrifugation d'une émulsion les parties d'abord sédi-mentées seront relativement plus riches en gros grains. Vous concevez ainsi qu'il soit facile de trouver une technique permettant de trier les grains selon leur taille par centrifugation fractionée. L'opération est d'ailleurs longue (j'y ai passé plusieurs mois), mais enfin ne demande que de la patience.

Une fois réalisée une émulsion à grains suffisamment uniformes, il faut déterminer le poids moyen de ces grains. Leur densité se mesure comme pour une poudre quelconque (le poids de résine en suspension dans le flacon employé se dose par simple dessiccation). Toute la difficulté est donc d'obtenir le diametre. Il semble indiqué de le mesurer au microscope par le procédé de la chambre claire, au
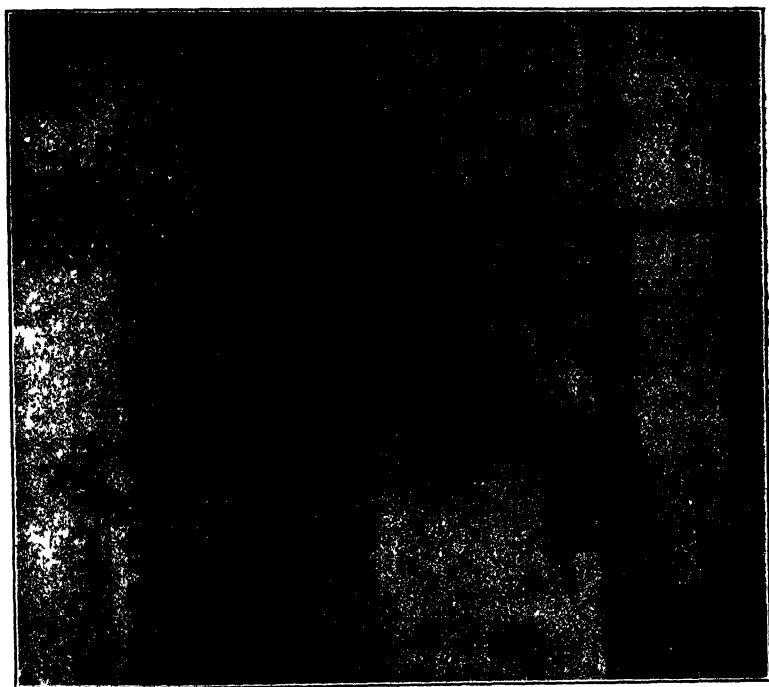
FIG. 2.

moyen d'un micromètre objectif. Mais les grains utilisables sont si petits qu'on ferait facilement ainsi des erreurs de 20 pour 100 et plus. Un procédé presque aussi direct consiste à laisser évaporer une gouttelette d'émulsion sur le micromètre objectif : il se trouve, comme vous pouvez voir ici sur une projection (Fig. 2), que les grains se disposent alors en alignements réguliers, dont cette fois on peut mesurer la longueur avec assez de précision. Divisant cette longueur par le nombre de grains, on a le diamètre.

Un autre procédé, plus long, mais plus précis, consiste à compter combien il y a de grains dans un volume connu d'émulsion titrée, ce qui donne la masse d'un grain, et, par suite, son rayon, puisque l'on connaît sa densité. J'ai utilisé pour cela le fait, accidentellement observé, qu'en milieu très faiblement acide les grains de gomme-gutte se collent sur le verre. A distance notable des parois, le mouvement brownien n'est pas modifié ; mais, sitôt que les hasards de ce mouvement amènent un grain au contact d'une paroi, ce grain s'immobilise. L'émulsion s'appauvrit ainsi progressivement, et, après quelques heures, tous les grains qu'elle contenait sont fixés. On peut alors compter à loisir tous ceux qui proviennent d'un cylindre de base arbitraire (mesurée à la chambre claire).

Enfin un troisième procédé, que je ne vous explique pas en détail, se fonde sur l'observation du temps nécessaire pour que la partie supérieure d'une colonne verticale d'émulsion (haute de plusieurs centimètres) se clarifie sur une hauteur donnée. Ce temps, nécessaire aux grains pour descendre, en moyenne, de cette hauteur, donne le diamètre par application de la loi de chute d'une sphère dans un fluide visqueux (Stokes).

Ces trois procédés concordent, et cela est nécessaire pour que nous puissions avoir confiance dans la précision de mesures qui portent sur un rayon inférieur au millième de millimètre.

Dispositif d'Observation.—Il nous faut maintenant réaliser un dispositif qui permette de connaître la répartition d'équilibre en fonction de la hauteur. Pour cela, dans une cuve plate, dont la profondeur est $\frac{1}{10}$ de millimètre, on place une goutte d'émulsion qu'on aplatit aussitôt par un couvre-objet qui ferme la cuve et dont on paraffine les bords pour éviter l'évaporation.

On peut, comme l'indique la figure, disposer cette cuve verticalement, le corps du microscope étant horizontal, et donner à la colonne verticale où peut se distribuer l'émulsion une hauteur de quelques millimètres. On voit alors les grains s'accumuler dans les couches inférieures et tendre vers une distribution d'équilibre (pratiquement atteinte après un ou deux jours) où la raréfaction progressive en fonction de la hauteur est manifeste, comme vous pouvez le voir sur une projection, qui rappelle de façon évidente la loi de raréfaction des gaz pesants.

Mais, si petits que soient nos grains, ils sont encore tellement

lourds que la raréfaction en est extrêmement rapide et que la hauteur sur laquelle on peut utilement faire des mesures est inférieure au dixième de millimètre.

On peut donc, comme on voit également sur la figure, laisser la cuve horizontale, le corps du microscope étant vertical, auquel cas il suffit d'un quart d'heure environ pour que la répartition d'équilibre s'établisse. L'objectif du microscope, très grossissant, a une faible profondeur de champ, et on ne peut voir nettement, a un même instant, que les grains situés dans une tranche horizontale tres mince dont l'épaisseur est peu supérieure au millieme de millimetre. Si l'on éleve ou abaisse le microscope, on voit les grains d'une autre tranche. La distance de ces deux tranches se déduit du déplacement vertical lu sur la vis du microscope ; le rapport des nombres de grains

OBJECTIF
MICROSCOPIQUE
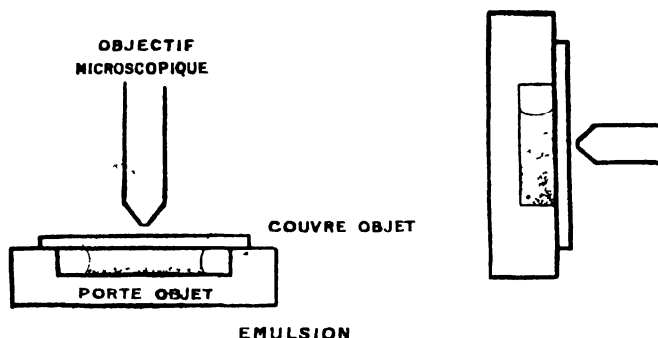
COUVRE OBJET

PORTE OBJET

EMULSION

FIG. 3.

aperçus donne donc la raréfaction qui correspond à une élévation connue. C'est sous cette forme que j'ai d'abord fait ces expériences.

Je n'étais pas sûr qu'il y aurait la moindre raréfaction, et pas davantage sûr que, au contraire, tous les grains ne se ramasseraient pas tout contre le fond. Or, j'ai vu s'établir un régime permanent de raréfaction bien régulière. Cette raréfaction est particulièrement frappante quand, tenant l'œil fixé sur la préparation, on soulève rapidement le microscope au moyen de sa vis micrométrique. On voit alors les grains se raréfier rapidement, comme fait l'atmosphère autour d'un aérostat qui s'élève.

Reste à faire des mesures précises. Quand on aperçoit dans le champ quelques centaines de grains qui s'agitent en tous sens ou disparaissent en même temps qu'apparaissent de nouveaux grains, on renonce vite à les compter. Heureusement, on peut faire des photographies instantanées des diverse tranches, et compter ensuite a loisir sur les clichés les nombres de grains présents dans ces tranches

Il est facile de vérifier ainsi que des élévations égales s'accompagnent de raréfactions égales. Par exemple, pour des grains de

rayon égal à 0,212 μ, trois bonds successifs de 30 μ abaissaient la concentration sensiblement à la moitié, au quart et au huitième de sa valeur.   Pour d'autres grains, de rayon égal à 0,367 μ, une élévation de 6 μ suffisait pour rendre la densité deux fois plus faible environ. Vous voyez ici précisément un dessin obtenu en plaçant juste au-dessous l'une de l'autre 5 coupes faites à 6 μ de distance dans cette émulsion (Fig. 4).

Pour obtenir la même raréfaction dans de l'air, nous avons vu qu'il faudrait faire un bond de 6 kilomètres, un milliard de fois plus grand. Si notre théorie est bonne, le poids d'une molécule d'air serait donc le milliardième du poids que pèse, dans l'eau, un de nos grains. Le poids de l'atome d'hydrogène s'obtiendra de même et tout l'intérêt de la question est maintenant de savoir si nous allons ainsi retrouver les nombres auxquels avait conduit la théorie cinétique.

Aussi, j'ai ressenti une vive émotion quand, dès le premier essai, j'ai en effet retrouvé ces nombres que la théorie cinétique avait obtenus par une voie si profondément différente. J'ai d'ailleurs varié autant que j'ai pu les conditions de l'expérience. Par exemple, la masse de mes grains a pris une série de valeurs échelonnées entre des limites qui sont entre elles comme 1 et 40 ; j'ai changé la nature de ces grains, opérant sur diverses résines (en particulier sur le mastic) ; par addition de glycérine, j'ai accru dans le rapport de 120 à 1 la viscosité du liquide intergranulaire, changeant en même temps la nature de ce liquide ; enfin j'ai notablement changé la densité apparente des grains, qui, dans l'eau, a varié du simple au quintuple, et qui est devenue négative pour de la gomme-gutte dans de la glycérine a 10 %

Fig. 4.

d'eau (dans ce dernier cas, les grains, plus légers que la liquide, s'accumulaient dans des couches supérieures).* Toujours j'ai obtenu
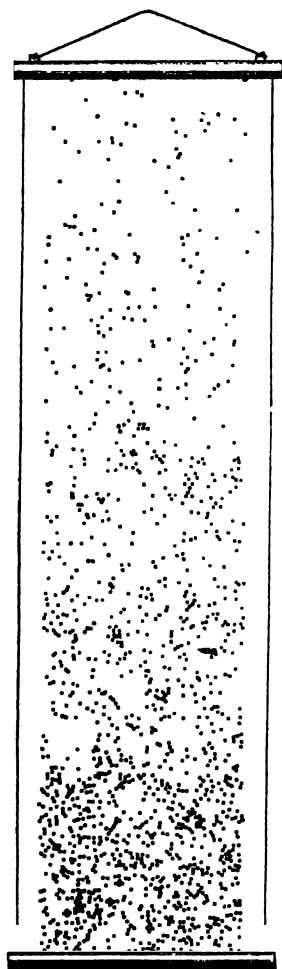
* Tout récemment enfin, sous ma direction, M. Bruhat a fait varier la température de −10° à +58°, et a encore ainsi retrouvé le même poids.

des résultats concordants, indiquant pour l'atome d'hydrogène un poids très voisin du poids $1,6 \cdot 10^{-24}$ donné par la théorie cinétique.

Je ne pense pas que cette concordance puisse laisser de doute sur l'origine du mouvement brownien. Pour comprendre à quel point elle est frappante, il faut encore une fois songer qu'avant expérience on n'eût pas osé certifier que la chute de concentration ne serait pas négligeable sur la faible hauteur de quelques microns, et que, par contre, on n'eût pas osé davantage affirmer que tous les grains ne se rassembleraient pas dans le voisinage immédiat du fond de la cuve. La première éventualité donnerait une valeur nulle, et la seconde une valeur infinie pour le poids de l'atome d'hydrogène. Que l'on soit tombé, avec *chaque* émulsion, dans *l'immense* intervalle qui semblerait donc *à priori* possible, précisément sur une valeur si voisine du nombre prévu, ne paraîtra sans doute pas l'effet d'une rencontre fortuite.

Mais il y a plus : tandis que la théorie cinétique en raison même des simplifications qui permettent ses calculs, donne, même à partir d'expériences parfaites, des résultats d'une approximation incertaine, les nombres donnés par les émulsions correspondent à une mesure véritable dont rien ne limite la précision. Par ce moyen nous saurons vraiment peser les atomes, et non pas seulement estimer grossièrement leur poids.

Les deux séries d'expériences que je regarde comme le plus sûres m'ont ainsi donné pour le poids de l'atome d'hydrogène (après dénombrement d'environ 30.000 grains), la valeur

$$\frac{1,47}{1.000.000.000.000.000.000.000.000}$$

ou, plus brièvement, $1^{gr},47 \cdot 10^{-24}$.

Les autres grandeurs moléculaires s'ensuivent. Par exemple, vous verriez aisément que dès lors il doit y avoir dans chaque centimètre cube d'air (conditions normales) 31 milliards de milliards de molécules, et que la charge élémentaire, ou électron, vaut $4,2 \cdot 10^{-10}$ (unités électrostatiques C.G.S.).

Les Grandeurs moléculaires peuvent se déduire du Degré d'Agitation.—Nous avons donc pu étendre, avec un plein succès, les lois des gaz aux émulsions, et du même coup obtenir les poids absolus des atomes. Il est remarquable que, dans ces mesures, nous n'avons pas eu à nous occuper de l'activité du mouvement brownien. Les lois des gaz sont vérifiées par les émulsions aussi bien dans la glycérine, où le mouvement brownien est à peine perceptible, que dans l'eau où il est très vif, la seule différence étant que la répartition d'équilibre se réalise beaucoup plus vite dans l'eau que dans la glycérine.

D'autre part, ce mouvement brownien, étudié en lui-même, va

nous donner un nouveau moyen d'atteindre les grandeurs moléculaires, moins intuitif peut-être que la précédent, mais aussi précis, et qui a été indiqué par *Einstein* en un très beau travail théorique (1905).

Sans chercher à suivre le trajet infiniment enchevêtré que décrit un grain pendant un temps donné, Einstein considère seulement son *déplacement* pendant ce temps, c'est à dire le segment rectiligne qui joint son point de départ à son point d'arrivée, et montre que, si certaines hypothèses fondamentales de théorie cinétique sont exactes, la connaissance de la valeur *moyenne* de ce déplacement permet d'obtenir les grandeurs moléculaires.

Je ne puis donner ici le détail de ce raisonnement, et me borne à dire que la principale hypothèse utilisée par Einstein consiste à supposer non seulement, comme on faisait déjà, qu' à la même température toutes les molécules ont la même énergie moyenne de mouvement, mais que même un grain déjà perceptible a encore la même énergie moyenne de mouvement. La formule d'Einstein donne alors cette énergie moléculaire moyenne, des que l'on connaît le déplacement moyen en un temps donné, dans un liquide ayant une viscosité connue, de grains sphériques de rayon connu. L'énergie moléculaire pourra donc s'obtenir par cette voie, et du même coup les masses des diverses molécules, car nous avons vu que l'on sait ce que doivent être leurs vitesses, pour que leurs chocs sur les parois expliquent les pressions observées.

Einstein fit remarquer que l'ordre de grandeur des déplacements observés concordait parfaitement avec la théorie, et laissa aux expérimentateurs le soin d'une comparaison plus précise. Puisque j'avais des grains ronds de diamètre connu, je me trouvais en état de faire cette comparaison, comme me le fit observer M. Langevin en me signalant la théorie d'Einstein que j'ignorais. Je confiai d'abord ces mesures à M. Chaudesaignes pour la gomme-gutte, à M. Dabrowski pour le mastic, puis je fis moi-même un grand nombre de pointés. Le résultat fut ·décisif et montra l'exactitude rigoureuse de la formule d'Einstein, le poids de l'atome d'hydrogène calculé par cette méthode se trouvant égal à $1,45.10^{-24}$ grammes, pratiquement identique au nombre que m'a donné la répartition en hauteur des émulsions.

Vous apercevez sur la projection ci-jointe, à un grossissement tel que 16 divisions du quadrillage représentent 50 microns, trois dessins obtenus en traçant les segments qui joignent les positions consécutives d'un même grain de mastic, de rayon égal à $0^\mu,52$, pointé de trente en trente secondes, à la chambre claire. C'est en faisant la moyenne de pareils segments qu'on peut vérifier la formule d'Einstein.

Ces dessins ne vous donnent au reste qu'une idée très affaiblie du prodigieux enchevêtrement de la trajectoire réelle. Si, en effet, on faisait des pointés de seconde en seconde, chacun de ces segments rectilignes se trouverait remplacé par un contour polygonal de trente côtés relativement aussi compliqué que le dessin ici reproduit, et ainsi de suite.

Pour varier les conditions, j'ai cherché et j'ai réussi à préparer des grains beaucoup plus gros que ceux qui m'avaient servi jusqu'alors. Pour cela, j'ai fait arriver lentement de l'eau, par un entonnoir à pointe effilée, sous une solution alcoolique de mastic. Les grains qui se forment alors dans la zone de passage ont couramment un diamètre d'une douzaine de microns, diamètre qui se mesure directement à la chambre claire, et sont donc environ 100.000 fois plus lourds que les plus petits de ceux qui m'avaient servi. Pour que ce poids ne les maintienne pas sans cesse au contact immédiat du fond, je les ai observés dans une solution d'urée qui a presque leur densité. J'ai ainsi constaté que la formule d'Einstein s'applique encore. Enfin j'ai pu éprouver une autre formule, également déduite par Einstein des
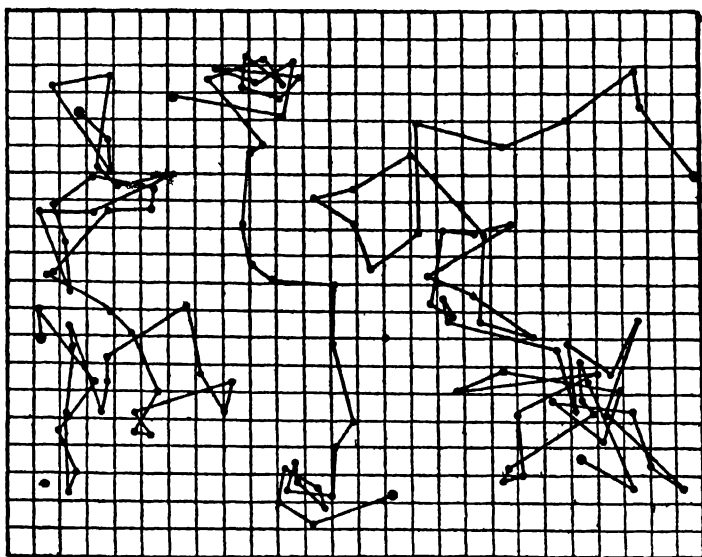

Fig. 5.

hypothèses moléculaires, et qui porte sur la rotation moyenne d'un grain en un temps donné. Cette formule prévoyant environ 100° de rotation par seconde pour des grains de l'ordre du micron, semblait difficilement vérifiable. Mais heureusement j'avais de gros grains ; en raison de la grosseur de ces grains, et parce que certains d'entre eux contiennent de petites inclusions qui servent de point de repère, *j'ai pu constater et mesurer leur rotation*. Les mesures, assez peu précises encore, m'ont donné $1,56.10^{-24}$ comme poids de l'atome d'hydrogène, en sorte que la légitimité de ce nouveau moyen d'atteindre aux grandeurs moléculaires n'est pas douteuse.

Je n'ai plus rien à vous dire sur mes recherches, mais vous me permettrez au moins de vous signaler d'autres méthodes, toutes récentes, qui ont également permis d'atteindre aux grandeurs moléculaires. Une d'elles, due à Lord Rayleigh, donne le nombre de molécules contenues dans une colonne d'air de masse calculable, d'après la diffraction qu'elles font subir à la lumière solaire, et qui, favorisant les couleurs plus réfrangibles, serait l'origine du $\cdot$ *bleu du ciel*. Pour avoir les grandeurs moléculaires, il suffit ainsi de mesurer en même temps, pour une même radiation, l'éclat du soleil et dans une direction connue, celui du ciel. Les mesures (Bauer et Moulin), qui ne compórtent pas une grande précision, à cause de la part difficilement calculable que les rayons réfléchis sur le sol prennent dans l'illumination du ciel, donnent pourtant un très bon ordre de grandeur, indiquant, à 50% près peut-être, $1,6.10^{-24}$ pour le poids de l'atome d'hydrogène.

Une autre méthode plus précise, se fonde sur la mesure des charges électriques transportées par des gouttelettes microscopiques. Ces charges sont généralement petites et sont des multiples entiers d'un même atome d'électricité, par la directement mesurable, qui se trouve égal à ce que peut charrier un atome d'hydrogene dans l'électrolyse. Comme on sait ce que transporte 1 gr. d'hydrogene, on a encore par là le poids de l'atome. Cette méthode, imaginée par Townsend et Sir J. J. Thomson, perfectionnée par H. A. Wilson et surtout par Millikan (qui a réussi à prouver de la façon la plus nette la structure atomique de l'électricité), donne actuellement des chiffres compris entre $1,4.10^{-24}$ et $1,7.10^{-24}$.

Un autre groupe de mesures a son origine dans les propriétés des corps radioactifs. Vous savez que certains de ces corps émettent des rayons a qui excitent la phosphorescence du sulfure de zinc. Sir William Crookes, en éxaminant à la loupe cette phosphorescence, la vit se résoudre en un fourmillement de scintillations éteintes aussitôt qu'apparues. Les rayons qui les excitent sont matériels, car partout où ils pénètrent, on constate bientot la présence d'hélium (Rutherford) : ils sont probablement formés par des atomes d'hélium chargés positivement. Sir W. Crookes a supposé que chaque scintillation marquait l'arrêt de l'un de ces atomes qui sont lancés à la vitesse prodigieuse de 20,000 kilomètres par seconde. Si l'on compte alors les scintillations dues en un temps donné a une masse connue de corps radioactif, et si l'on mesure le volume d'hélium dégagé pendant le même temps, on saura combien ce volume contient d'atomes et les grandeurs moléculaires s'ensuivront. On peut également (je n'insiste pas sur ce point, simplement pour abréger) mesurer la charge positive rayonnée, ou la fraction détruite du corps radioactif. Ces admirables experiences conduisent, pour le poids h de l'atome d'hydrogène, à des nombres compris entre $1,4.10^{-24}$ et $1,6.10^{-24}$.

Je ne puis enfin que vous indiquer l'existence des belles théories par lesquelles Planck et Lorentz ont relié les grandeurs moléculaires

à la répartition de l'énergie dans le spectre d'un corps incandescent. Les mesures, qui pourront devenir très précises, donnent dès maintenant pour h le poids $1,6 \cdot 10^{-24}$.

Je pense que vous serez frappés de la diversité des routes qui conduisent ainsi à un même résultat. Si nos hypothèses étaient fausses, chacun de ces phénomènes pourrait donner n'importe quel jeu de valeurs échalonnées entre zéro et l'infini. Par exemple, en ce qui regarde le mouvement brownien, la mesure des déplacements moyens donnerait des nombres différents avec de gros grains et avec de petits grains. Ces valeurs n'auraient d'ailleurs aucun rapport avec celles, également variables, que donneraient les répartitions en hauteur. Qu'il y ait convergence, non seulement à l'intérieur de chaque méthode, mais entre toutes les méthodes ; que des phénomènes aussi profondément différents que la viscosité des gaz, le mouvement brownien, le bleu du ciel, l'électrisation de gouttelettes, la radioactivité, la répartition d'énergie dans le spectre, expriment tous la discontinuité de la matière et imposent tous les mêmes grandeurs pour les éléments de cette matière, *c'est cela qui est la démonstration de la réalité objective des molécules.* Peut être aussi trouverez-vous que ces concordances merveilleuses donnent un assez bon exemple des satisfactions que l'amour des belles choses trouve dans l'étude des sciences.

<div style="text-align: right">[J. P.]</div>

A New Method of Chemical Analysis.

I have had on several occasions the privilege of bringing before the
Members of the Royal Institution some of the results of the ex-
periments on the positive rays on which I have been engaged for the
last few years. I wish this evening to draw your attention to some
applications of these to various chemical problems.

The first application I shall consider is the use of these rays to
determine the nature of the gases present in a vacuum tube, to show
how they can be used to make a chemical analysis of these gases—an
analysis which, as we shall see, will enable us to determine not merely
whether an element. say, for example, oxygen, is present in the tube,
but will tell us in what form it occurs, whether, for example, it is
present in the atomic as well as the molecular condition, and whether
there are allotropic modifications present, such as ozone, O_3, and other
still more complex aggregations.

The method is as follows : the positive rays after passing through
a fine tube in the cathode are exposed simultaneously to magnetic
and electric forces, the magnetic field being arranged so as to produce
a vertical deflection of the rays, while the electric field produces a
horizontal .deflection. Thus, if when neither electric nor magnetic
fields are present, the rays strike a screen placed at right angles to
their direction at a point O, they will, when both electric and magnetic
forces are at work, strike it at a point P, where the length of the
vertical line P N is equal to the deflection produced by the magnetic
field, and the horizontal line O N to that produced by the electric field.

We know from the theory of the action of electric and magnetic
fields on moving electrified particles, that

$$P N = A \frac{e}{m v} \qquad O \cdot N = B \frac{e}{m v^2}$$

where A and B are constants depending on the strength of the
magnetic and electric fields and the geometrical data of the tube, e is
the charge on the particle, m its mass, and v its velocity.

From these relations we see that

$$\frac{m}{e} = \frac{A^2}{B} \frac{O N}{P N^2}$$

When these rays strike against a photographic plate, they affect the plate at the point against which they strike, and thus when the plate is developed we have a permanent record of the deflections of the rays. The methods of taking these photographs and the details of the experiment are described in my paper in the 'Philosophical Magazine,' Feb. 1911. The values of A and B can be determined accurately by the methods I have given in previous papers, and hence if we measure on the photographs the values of O N and P N, we can determine the value of m/e. If we wish to compare the values of m/e for two different rays, it is not necessary to determine A and B, all we have to do is to measure the values of O N and P N ; and thus the photograph alone gives us the means of comparing the value of m/e.

For the same type of carrier m/e is constant, so that $\dfrac{P N^2}{O N}$ is constant whatever may be the velocity, and therefore the locus of P, i.e. the curve traced on the photographic plate by this carrier, is a parabola. The reason we get a curve instead of a point is that the rays are not all moving with the same velocity, and the slower ones suffer greater deflection than the quicker ones. Each type of carrier produces its own line on the plate, and there are as many curves on the plates as there are kinds of carriers ; from an inspection of the plates we can find not merely the number of kinds of carriers, but from the dimensions of the curves we can at once determine the atomic weight of the carrier, and thus determine its nature. This is one of the great advantages of this method. To illustrate this advantage, let us compare the method with that of spectrum analysis. If the spectroscopist observes a line unknown to him in the spectrum of a discharge tube, the most he can deduce without further investigation is that there is some unknown substance present in the tube, and even this would be doubtful, as the new line might be due to some alteration in the conditions of the discharge. But if we observe a new curve in the positive ray spectrum, all we have to do is to measure the curve and then we know the atomic weight of the substance which produced it. To take an example, I have photographed the positive ray spectrum for nitrogen prepared from the atmosphere and that for nitrogen prepared from some nitrogenous compounds, and have found that the former contains a line * which is not in the latter, and that the value of m/e for this line is 40 times that for the atom of hydrogen. We thus know that atmospheric nitrogen contains an element of atomic weight 40, which is not present in chemical nitrogen—this element is, of course, argon. We might by ordinary spectrum analysis have found lines in the spectrum of atmospheric nitrogen which are not in the spectrum of chemical

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* As a matter of fact, there is a second, very faint line for which m/e is about 20 times that for the atom of hydrogen. This is probably due to an atom of argon with two electric charges.

nitrogen, and might thus have suspected the presence of another element, but spectrum analysis could not tell us anything about the nature of this element, whereas the positive ray spectrum at once gives us its atomic weight.

The positive-ray method is even more delicate than that of spectrum analysis, for by it we can detect the presence of quantities of a foreign gas too minute to produce any indication in the spectroscope. I have, for example, often been able to detect the presence of helium by this method, when no indication of its presence could be detected by a spectroscope.

Again, when a line in the positive-ray spectrum can be seen, the atomic weight of the carrier which produces it can be determined with great accuracy. Though the method is only a few months old, it is even now sufficiently developed to determine with an accuracy of 1 per cent. the atomic weight of a gaseous substance, without requiring more than $\frac{1}{100}$ milligramme of the substance. Another very important advantage of this method is that it is not dependent upon the purity of the material; if the material is impure the impurities merely appear as additional lines in the spectrum, and do not affect the parabola due to the substance under examination, and therefore produce no error in the determination of the atomic weight. The method would seem to be peculiarly suitable for the determination of the atomic weights not merely of the emanation from radio-active substances, but also those of the products into which they disintegrate.

The rays, too, are registered within less than a millionth of a second after their formation, so that when chemical combination or decomposition is occurring in the tube, the method may disclose the existence of intermediate forms which have only a transient existence, as well as of the final product, and may thus enable us to gain a clearer insight into the process of chemical combination.

I will now show a few slides prepared from photographs we have taken of the positive-ray spectra. The first is that of nitrogen prepared from air ; the measurements of the photograph showed that the atomic weights of the carrier producing these curves were as follows :—

Positive.		Negative.	
1	H_+	1	H_-
1·99	H_{2+}	11·20	C_-
6·80	N_{++}	15·2	O_-
11·40	C_+		..
13·95	N_+		..
28·1	N_{2+}		..
39	Arg_+		..
100	Hg_{++}		..
198	Hg_+		..

The symbol H_+ denotes that the carrier is an atom of hydrogen

with one charge ; H_{2+} that it is a molecule of hydrogen with one charge ; N_{++} that it is an atom of nitrogen with two charges ; and so on.

With nitrogen from NH_4NO_2 the lines were as follows (the magnetic force was so large that some of the lines corresponding to the lighter particles were thrown off the plate) :—

$6 \cdot 1$	C_{++}^-	$44 \cdot 2$	CO_{2+}
$7 \cdot 02$	N_{++}	$65 \cdot 5$	$Hg_{+++}(?)$
$12 \cdot 08$	C_+	100	Hg_{++}
$14 \cdot 01$	N_+	201	Hg_+
$27 \cdot 9$	N_{2+}		

The next slide is the positive-ray spectrum for CO, and again the magnetic field is so great that the lighter carriers do not appear.

From the measurement of the lines we find that the atomic weight of the carrier is—

Positive.		Negative.	
$6 \cdot 00$	C_{++}	12	C_-
$6 \cdot 95$	N_{++}	16	O_+
$7 \cdot 95$	O_{++}	$..$	
$12 \cdot 02$	C_+	$..$	
$13 \cdot 9$	N_+	$..$	
$15 \cdot 95$	O_+	$..$	
$28 \cdot 05$	CO_+	$..$	
43	CO_{2+}	$..$	
$69 \cdot 5$	$Hg_{+++}(?)$ very faint	$..$	
100	Hg_{++}	$..$	
202	Hg_+	$..$	

The spectrum for CO_2 is represented in Fig. 6 ; the atomic weights are :—

$5 \cdot 98$	C_{++}	$43 \cdot 9$	CO_{2+}
$8 \cdot 00$	O_{++}	$62 \cdot 5$	Hg_{+++} (?) very faint
$12 \cdot 00$	C_+	$99 \cdot 6$	Hg_{++}
$16 \cdot 00$	O_+	$200 \cdot 0$	Hg_+
$28 \cdot 02$	CO_+		

The spectrum of CH_4, of which a small region with five lines close together is shown in Fig. 4, is interesting, because the measurement of these lines shows that their atomic weights are 12, 13, 14, and 15, 16, and thus that we have here C, CH, CH_2, CH_3, CH_4. If I am not mistaken, this is the first occasion when the atoms CH, CH_2, CH_3, have been observed in a free state.

The spectrum of the analogous compound chloroform $CHCl_3$

is represented in Fig. 7.   The atomic weights represented in this are :—

1	H_+	18·5	Cl_{++}
1·5	(?)	27·7	CO
2	H_{2+}	36·0	Cl_+
3	(?)	46·5	CCl_+
6	C_{++}	63	(?) faint
8	O_{++}	81	CCl_{2+}
11·9	C_+	102	Hg_{++}
13·7	N_+	201	Hg_+
16·0	O_+		

The carriers with atomic weights 1·5 and 3 have not been iden-tified.   They are of frequent occurrence.   I have here two slides, one of SiH_4 and the other of the residual gas in tube after the air has been pumped out, in which they are well marked, though at their best they are only faint lines.

Let us now consider some of the results brought to light by these photographs.   In the first place, they show that a gas through which an electric discharge is passing is a much more complex thing than a collection of molecules all equal to each other.   Even an elementary gas becomes under these circumstances a mixture of a great many different substances.   Thus, to take oxygen as an example, the photographs show that when a current of electricity passes through it, we may have present simultaneously oxygen in the following states :—

1. Ordinary molecular oxygen, O_2.
2. Neutral atoms of oxygen, O.
3. Atoms of oxygen with 1 positive charge, O_+.
4. Atoms of oxygen with 2 positive charges, O_{++}.
5. Atoms of oxygen with 1 negative charge, O_-.
6. Molecules of oxygen with 1 positive charge, O_{2+}.
7. Ozone with a positive charge, O_{3+}.
8. O_6 with a positive charge, O_6.

And, in addition, there are free negative corpuscles.   Thus in the elementary gas there are at least nine (the list has no claim to be exhaustive) separate substances present when the discharge passes through it.   Each of these substances has almost certainly different properties, possibly a characteristic spectrum.   If we took any other gas we should find that the same thing would be true : thus in hydrogen we have H, H_2, H_+, H_-, H_{2+}, even if we do not ascribe to hydrogen the lines giving $m/e = 1·5$ or 3.   In nitrogen we have N, N_2, N_+, N_{++}, N_{2+}, carbon occurs as C_+, C_{++}, C_-, chlorine as Cl, Cl_2, Cl_+, Cl_{++} and Cl_-, mercury as Hg, Hg_+, Hg_{++}, and pro-bably as Hg_{++}, as there is a very persistent line for which m/e is about 66.

Thus, whenever the electric current passes through a gas, and probably whenever a gas is ionized, the gas becomes a mixture of many different substances. We can thus readily understand why in the spectra of many elements many of the lines may be grouped together so as to form different series—the principal series, the first co-ordinate series, and so on—and the spectrum of the discharge-tube regarded as the superposition of a number of different spectra whose relative intensities may be subject to very great variations. This, indeed, is just what would happen if some or all of the sub-stances which are present when the gas is in the ionized state gave rise to different spectra.

Another feature which I think is of great interest from the point of view of the theory of chemical combination is the occurrence of particles with negative charges. Let us consider for a moment how these are formed. They are formed after the particles have passed through the cathode ; the path between the cathode and the photo-graphic plate contains abundance of corpuscles produced by the ionization of the gas : a neutral particle after passing through the cathode picks up a negative corpuscle and so becomes negatively charged. For this to occur the attraction between the corpuscle and the neutral particle must be exceedingly strong, for it is not a question of a particle at rest attracting to itself a negatively electrified corpuscle sauntering about in its neighbourhood ; in our case the neutral particle is rushing past the corpuscle with a velocity of the order of 10^8 cm. per sec. In order that the particle may under these circumstances be able to drag the corpuscle along with it, the attraction between the two must be so great, that to move a corpuscle against this attraction from the surface of the particle away to an infinite distance must require an amount of work of the same order as that required to communicate to the corpuscle a velocity of 10^8 cm. per sec. : this is equal to the work required to move the atomic charge against a potential difference of about 3 volts, and is therefore comparable with the work required to dissociate some of the most stable chemical compounds.

The fact, then, that some particles get negatively charged shows that in the neutral state these particles have an exceedingly strong affinity for a negatively electrified particle, while the absence of a particular particle from the negative side shows that its affinity is much less, but does not imply that it vanishes altogether. From what we have said, it should follow that the more slowly the neutral par-ticles are moving relatively to the corpuscles, the more easily will the negatively electrified systems be formed. This is confirmed in a very striking way by our experiments, for when the discharge is .passing very easily through the tube, and the velocity of the neutral particles is relatively small, the number of negatively electrified particles is very much increased ; indeed, in some cases the brightness of the part of the photograph corresponding to the negative particles
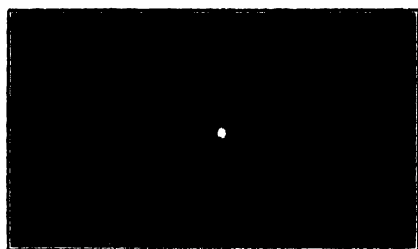
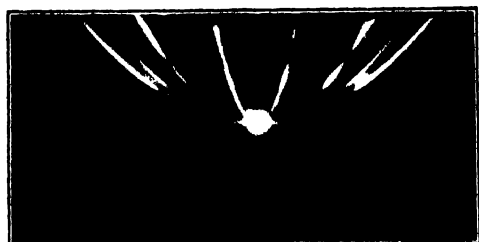Fig 1   Nitrogen from air

Fig 2   Air

Fig. 3.   CO

Fig. 4.   CHCl₃.

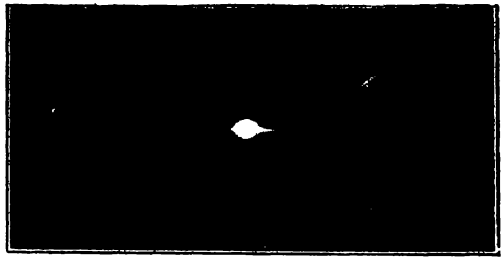*As these figures are printed, the magnetic deflectio*
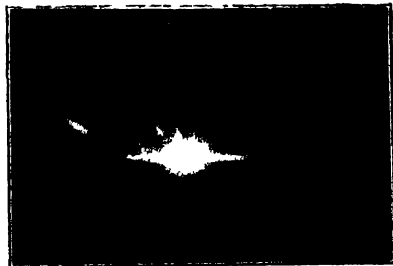
Fig 5   CH₄

Fig 6   CO₂.

Fig. 7.   SiH₄.

horizontal, the electrostatic deflections vertical.

is as great as that corresponding to the positive, whereas when the discharge is passing with great difficulty, and the velocity of the neutral particles is very high, the negative part is very faint compared with the positive.

The particles which have been observed on the negative side are the hydrogen atom, the carbon atom, the oxygen atom, and the chlorine atom. The presence of the oxygen and chlorine atoms might, perhaps, have been expected, as these are universally regarded as strong electro-negative elements, i.e. as elements which have a strong affinity for negative electricity. The presence of the hydrogen atom is more remarkable, for hydrogen is generally considered to be a strongly electro-positive element, yet on these photographs we find it more persistently on the negative side than any other particle : often when no other line on the negative side is strong enough to be detected, the line corresponding to the hydrogen atom is distinctly visible. This is all the more remarkable, because the hydrogen atom, being the lightest of all the particles, is moving with the greatest velocity relatively to the corpuscles, and therefore would, other circumstances being the same, be the least likely to capture them. The heavier the particle, the slower is its velocity, and the greater chance it has of capturing the corpuscles ; the fact that heavy complicated particles are conspicuous by their absence on the negative side shows that the attraction of these for the corpuscles must be exceedingly small compared with that exerted by a neutral atom of hydrogen. It will be seen that the atom of carbon, also regarded as an electro-positive element, is also conspicuous on the negative side.

On looking at the list of the particles which occur on the negative side, we are struck by the fact that they are all atoms : there is not a molecule among them. Thus, although the curve corresponding to the negatively electrified hydrogen atom occurs on every plate, there is not a single plate which shows a trace of a curve corresponding to a negatively electrified hydrogen molecule, although that corresponding to the positively electrified molecule is always present, and on some of the plates is stronger than that due to the positive hydrogen atom. Again, on some plates the positive oxygen molecule shows stronger than the oxygen atom, but on the negative side only the atom is visible.

Thus neutral atoms, but not neutral molecules, can exert on the negative corpuscles those enormous attractions which, under the conditions of these experiments, are required to bind the corpuscles to these rapidly moving particles. We may compare this result with the properties ascribed by chemists to bodies when in the nascent condition, i.e. when they have only recently been liberated from chemical combination, and when they are likely to be partly in the atomic state ; for atoms, as we have seen, exert forces on electric charges in their neighbourhood vastly greater than those exerted by molecules.

We may compare the forces exerted by a neutral atom on the

corpuscles with those exerted by an unelectrified piece of metal on a charged body in its neighbourhood. In consequence of electrostatic induction, the charge and the metal will attract each other. This attraction is dependent on the electricity in the metal being able to move under the electric forces exerted by the charge, and to re-arrange itself in such a way that if the charge is positive, the negative electricity in the metal moves to the part of the metal nearest to the charge, while the positive electricity moves to the part remote from the charge. The force between the metal and the charge depends on the freedom of the electricity to move about in the metal under the action of the electric field. If the metal is replaced by a substance of high specific inductive capacity, like sulphur, in which the electricity has an appreciable amount of free-dom, though not so great as in a metal, the attraction, though still appreciable, is very much less than it was with the metal. A very simple experiment will illustrate this point. I have on this card-board disk, which is suspended from a long string, a number of magnets, such as are used for compasses ; if I mount the magnets on pivots, so that they are free to turn round, the system of magnets is strongly attracted when another magnet is brought near it ; if, how-ever, I take the magnets off their pivots so that they are no longer free to turn, the magnet exerts very little attraction upon them.

A view of chemical combination which I gave some time ago in the ' Philosophical Magazine,' and also in my Corpuscular Theory of Matter, suggests that there is a very close analogy between the causes at work in the experiment we have just made and those which pro-duce the difference between the behaviour of atoms and molecules. On that theory the atom was supposed to consist of a large number of corpuscles arranged inside a sphere of positive electricity ; the corpuscles arranging themselves so as to be in equilibrium under their mutual repulsion and the attraction of the positive electricity. The configuration depends on the number of corpuscles, and the stiffness and stability of the system also change as the number changes. For some particular numbers of corpuscles the system is very rigid, and any movement of the corpuscles would be strongly resisted ; since the movement of electricity inside the atom is brought about by the movement of the corpuscles, the electricity could only move with great difficulty inside these atoms, and they would therefore not be able to exert more than feeble forces on electrical charges outside the atom : they would therefore not enter readily into combination with other atoms. We may ascribe such a constitu-tion as this to the atoms of the inert gases, helium, argon, and neon. A system with one, two, or three more corpuscles than the system ·we have just described would not be nearly so stable, and there would be a tendency to discard the extra corpuscles from the atom so that it might return to the more stable form. We may roughly picture to ourselves the atom with one extra corpuscle as consisting

of a number of fixed corpuscles plus one which is free to move about ; the freedom of this corpuscle would enable the electricity in the atom to move about, and would endow the atom with the property of attracting any electrical charges which might be near it.   If there were two corpuscles in the atom more than the number required for the most stable form, we can picture the atom as having two corpuscles free and the rest fixed.   Similarly, if we had more than two extra corpuscles.   Thus we may regard the atom as possessing 0, 1, 2, 3 corpuscles which are able to move about with more or less facility, and the free corpuscles will give to the atom the power of exerting attractions on electrical charges to an extent which depends on both the number of corpuscles and the freedom with which they can move about.   On the theory to which I have alluded the number of these "free" corpuscles determines the valency of the atom.

Now let us suppose that two such atoms come into such close connexion that the corpuscles in the one exert considerable forces on those in the other.   The system consisting of the two atoms will rearrange itself so as to get into a more stable form, if necessary corpuscles passing from one atom to the other to enable it to do so. The greater stability, however, implies a loss of mobility ; the free corpuscles have become parts of a more stable system, and have therefore lost to a greater or less extent their mobility.   But with the mobility of the corpuscles goes their power of exerting forces on electrical charges ; and thus the combination of the atoms diminishes to a great extent the attractions they exert outside them.   Speaking generally, we may say that on this view the combination of atoms to form molecules, either of compounds or elements, fixes corpuscles which were previously mobile and converts the atoms from conductors of electricity into insulators with a small specific induction capacity.

I have brought these illustrations before you with the object of showing that we have now methods which are capable of dealing with much smaller quantities of matter than the methods now used by chemists, methods which are capable of detecting transient phases in the processes of chemical combination, and which I am hopeful may be of service in throwing light on one of the most interesting and mysterious problems in either physics or chemistry—the nature of chemical combination.

[J. J. T.]

Friday, May 5, 1911.

SIR WILLIAM CROOKES, O.M. LL.D. D.Sc. F.R.S., Honorary
Secretary and Vice-President, in the Chair.

PROFESSOR MARTIN O. FORSTER, D.Sc. PH.D. F.R.S. *M.R.I.*

New Organic Compounds of Nitrogen.

[WITH EXPERIMENTAL ILLUSTRATIONS.]

IT may be stated without fear of contradiction that the most versatile
form of elemental matter is nitrogen. Rivalled only by argon and
its associates in reluctance to take part in chemical action, its entrance
into combination with other elements leads to interesting forms of
activity in great profusion. Union with hydrogen in different pro-
portions, for example, produces ammonia, hydrazine and hydrazoic
acid, three highly reactive substances having characteristics which
stand in marked contrast with one another. If oxygen be brought
into the system, hydroxylamine, nitrous acid and nitric acid may be
mentioned as typical materials capable of entering into chemical
changes of the most diverse order.

Organic derivatives of nitrogen, however, present an even greater
display of individuality. Prussic acid, the alkaloids, nitro-glycerine,
gun-cotton, celluloid, artificial musk, lyddite, indigo, the azo-dyes,
hæmoglobin and the enzymes are a few of the conspicuous nitrogen
compounds which suggest themselves in this connection, and a survey
of their activities would justify a reference to nitrogen as

" An element so various it seems to be
Not one, but all Hermetic Art's epitome."

It is not the occasion, however, to discuss the foregoing materials,
my present purpose being rather to deal with some new organic deri-
vatives of nitrogen which, although not associated with any important
industrial development, nevertheless display properties of considerable
interest to chemists.

The extraordinary inertness of elemental nitrogen has been already
mentioned, and the underlying cause of this feature is the tenacity
with which two atoms of the substance remain in combination with
each other. But in circumstances which will be explained later, three
atoms of nitrogen may be brought into and maintained in combina-
tion, the resulting complex being known as the triazo-group. It is a
remarkable fact that although, as has just been seen, nitrogen is dis-

tributed among naturally occurring substances almost as widely as carbon itself, there is no recorded example of a triazo-compound being obtained from natural sources. Clearly then, the union of atoms in the triazo-group is not among those marriages which are made in Heaven.

That being the case, it becomes necessary to consider the materials and processes which underly the synthetical production of triazo-compounds. Proceeding from ammonia, and replacing one of the hydrogen atoms by an amino-group, diamide, or hydrazine, is produced, but although discovered by Curtius in 1887, the method by which he prepared it is of historical interest only, it having been left to the ingenuity of Raschig, as recently as 1907, to accomplish the production of this substance by a simple and inexpensive process. This consists in first replacing an atom of hydrogen in ammonia by an atom of chlorine, and then, by direct action of more ammonia on the resulting chloramine, replacing the halogen by an amino-group :

$$NH_3 + NaOCl = NH_2Cl + NaOH.$$
$$NH_3 + NH_2Cl = NH_2 \cdot NH_2, HCl.$$
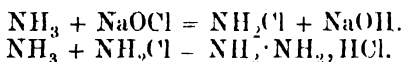
The new process illustrates in remarkable fashion the effect which physical condition may exert on chemical change. Although chloramine and ammonia may act together as already shown in a constructive direction, an alternative, destructive course is open to them, which is accelerated if the viscosity of the liquid is diminished :

$$2NH_3 + 3NH_2Cl = N_2 + 3NH_4Cl.$$
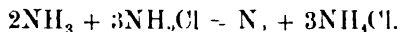
Thus Raschig was able to increase the yield of hydrazine by increasing the viscosity of the solution with addition of glue, whilst the undesirable effect, namely, liberation of nitrogen, was shown to follow the addition of acetone.

Just as ammonia may be doubled on itself to produce diamide or hydrazine, the latter might be expected to allow one of its hydrogen atoms to be replaced by another amino group and furnish triamide, or triazane. This, however, has not been accomplished, and there is evidence to suggest that such a substance would be most unstable. Whenever attempts are made to add another nitrogen link to the chain of two atoms in hydrazine, the terminal atoms of the three-link chain are found to have combined with one another, forming an enclosed association or ring of atoms. This is the triazo-group, and its simplest known form is the compound with hydrogen called azoimide, or hydrazoic acid, HN_3. The latter name emphasises the first point of interest in connection with the triazo-group. Whereas the simpler compounds of nitrogen with hydrogen, namely, ammonia and hydrazine, are both strong bases, forming very stable salts with acids, azoimide is a well-defined acid, forming salts with bases including ammonia and hydrazine themselves, the products then having com-

position expressed by the curious formulæ, N_4II_4 and N_5H_5. Another salt, that with ferric iron, provides a very delicate test for hydrazoic acid, the red colour being noticeable in solutions containing only one part per million.

Hydrazoic acid, discovered in 1890, also by Curtius, may be shown by experiment to follow an attempt to add another atom of nitrogen to hydrazine. Whilst the action of nitrous acid on ammonia causes both atoms of nitrogen to be liberated in elemental form,

$$HNO_2 + NH_3 - N_2 + 2H_2O,$$
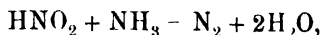
hydrazine is converted by the same agent into hydrazoic acid,

$$IINO_2 + NII_2 \cdot NII_2 = HN_3 + 2II_2O.$$

This process, however, is not adapted to the production of hydrazoic acid or its salts in large quantities. Two methods are available for this purpose. One of these, due to W. Wislicenus (1892), consists in passing a current of dry nitrous oxide over shallow layers of powdered sodamide at about 200°, and by means of certain modifications good yields of sodium azide may be obtained :

$$NaNH_2 + N_2O = NaN_3 + II_2O.$$
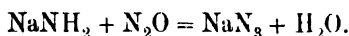
A later method, elaborated by Stollé and Thiele working independently (1908) is based on the experiment just mentioned, namely, the action of nitrous acid on hydrazine, but instead of using free nitrous acid, an ethereal nitrite, such as ethyl or amyl nitrite, is employed. These materials, in presence of alkali, transform hydrazine into sodium azide, the yield being excellent; and this discovery has resulted in the commercial production of that salt, which may now be purchased at less than 40s. per pound,

$$NH_2 \cdot NH_2 + Alk \cdot ONO + NaOEt = NaN_3 + Alk \cdot OII + EtOII + II_2O.$$
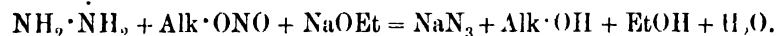
The free acid is a dangerous and disagreeable substance to manipulate. When free from water, it condenses to a colourless mobile liquid, which boils at about the same temperature as ether (37) ; but although harmless looking, it is a frightful explosive, and requires but slightly elevated temperatures for the display of this property. Moreover, the vapour is extremely poisonous, and when inhaled in even trifling quantities causes distressing headache ; it is, in fact, a powerful protoplasmic poison, its activity in this direction being comparable with that of prussic acid. As might be expected, therefore, its effect on the blood-spectrum is immediate and pronounced.

To chemists, however, the most conspicuous property of hydrazoic acid is the resemblance it bears to the halogen acids, a solution containing only one part per million giving a faint turbidity with silver nitrate. The resulting silver azoimide, in common with other hydrazoic salts of heavy metals, is dangerously explosive, but the salts of

the alkali metals may be handled without risk.   The latest recruit to
the metallic azoimides is radium azide, described by Ebler about six
months ago, and utilized in attempts to prepare metallic radium,
which appears to follow the decomposition of radium azide by heat,
just as barium azide may be shown to yield the metal when deprived
of nitrogen.   Pursuing the analogy between the triazo-group and the
halogen atoms, a study of the refrangibility and dispersion of light
by organic triazo-compounds deserves attention.   The following
measurements have been carried out by Philip, and show that while
the mean increment of refraction for an atom of bromine is 8·93,
that of the triazo-group is 8·91, and whilst the atomic dispersion of
bromine is 0·35, the increment traceable to the azoimide nucleus
is 0·36.

	Contribution of N_3-Group to	
	Refraction.	Dispersion
Ethyl Triazoacetate.	8·74	0·35
Ethyl α-Triazopropionate	8·87	0·36
Ethyl β-Triazopropionate	8·86	0·37
Ethyl Bistriazoacetate	9·07	0·38
Triazoethyl Alcohol	8·97	0·35
Bistriazoethane	8·98	0·36
Benzylazoimide	8·85	0·35
Contribution of N_3 (mean) . .	8·91	0·36
Contribution of Br	8·93	0·35

Moreover, on comparing the temperatures at which a number
of typical triazo-compounds boil with the constants for halogen
derivatives having similar structure, it appears that the triazo-group
exerts an elevating effect considerably greater than that of chlorine,
somewhat greater than that of bromine, and approximating to that
of iodine.   Furthermore, it has been shown by Philip that the intro-
duction of a triazo-group into a molecule of acetic acid has an effect
on the strength of the acid which is rather less than that due to a
bromine atom and rather greater than that caused by an iodine atom.

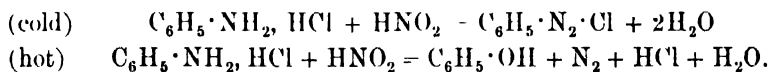|	Dissociation Constant.
Acetic Acid	0·000018
Iodoacetic Acid	0·00075
Triazoacetic Acid	0·00093
Bromoacetic Acid	0·00188
Chloroacetic Acid	0·00155
α-Triazopropionic Acid	0·00086
α-Bromopropionic Acid.	0·00108

Thus the physical evidence supports the chemical indications, and serves to classify the triazo-group as a complex radicle with a strong family resemblance to the halogens.

Bearing this resemblance in mind, it was natural to anticipate the possibility of constructing a composite molecule in which the azoimide nucleus is united with one atom of a halogen, for example chlorine, just as molecular chlorine is composed of two similar atoms. Such a synthesis has been lately accomplished by Raschig (1909), by the interaction of hypochlorous and hydrazoic acids,

$$HClO + HN_3 = ClN_3 + H_2O,$$
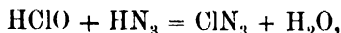
but the union between the two components is very easily broken, and chloroazoimide is highly explosive.

Proceeding now to study the behaviour of the triazo-group when placed in an organic environment, it is necessary first to examine the operations by which typical organic azoimides may be prepared. Although too numerous to be even summarised on the present occasion, some points in connection with the changes involved require attention. We have seen that the action of nitrous acid on ammonia sets free completely the nitrogen present in both materials. If, instead of ammonia there is taken its benzene derivative, aniline, in the form of the hydrochloride, nitrogen becomes added to that of the aniline, and although it is true that the product, when heated, gives up all its nitrogen just as ammonium nitrite does, the intermediate compound is perfectly stable at the temperature of melting ice :—

(cold) $\quad C_6H_5 \cdot NH_2, HCl + HNO_2 - C_6H_5 \cdot N_2 \cdot Cl + 2H_2O$

(hot) $\quad C_6H_5 \cdot NH_2, HCl + HNO_2 = C_6H_5 \cdot OH + N_2 + HCl + H_2O.$

This intermediate compound and related substances are among the most important, from both practical and theoretical standpoints, known to chemists. They are called diazonium salts, and their discovery, with that of many remarkable changes undergone by them, is due to Peter Griess (1858). It is not the least illuminating feature of Griess's work that the study of the diazo-compounds, underlying as it does the immensely valuable coal-tar colour industry, was pursued by its author while employed as chemist in a well-known firm of brewers, to whose particular undertaking the work in question had no application ; such far-sighted encouragement of apparently useless research for its own sake is an object lesson which is not, unhappily, without value even in these days.

Fascinating as are the problems, solved and unsolved, within the boundaries of diazo-chemistry, it would be inappropriate to encroach on them this evening, but the diazo-compounds forming a natural stepping-stone to the triazo-derivatives, it is relevant to draw passing attention to one recent application of their activity. The great class

of artificial colouring matters known as aniline dyes depend largely, though by no means exclusively, upon the process known to chemists as "coupling." If an aromatic base which has been treated with nitrous acid is added to one which has not been so diazotized, combination usually takes place in such a manner that a derivative of azobenzene is produced, and in the factory or laboratory coupling is effected with aqueous solutions maintained at zero to avoid decomposition of the diazo-group. A class of substances recently described by Morgan and Micklethwait, however, make it possible to administer the diazo-complex in a solid form, thereby greatly facilitating a demonstration of the coupling process; on mixing a few decigrams of toluene-p-sulphonyl-p-phenylenediazoimide with the same quantity of a-naphthylamine, adding a few c.c. of pyridine, and diluting the solution with absolute alcohol, concentrated hydrochloric acid develops an intense permanganate coloration.

We now arrive at the stage immediately preceding the organic triazo-compounds. Just as hydrazine itself, when treated with nitrous acid gives hydrazoic acid or azoimide, so phenylhydrazine with nitrous acid gives phenylazoimide,

$$C_6H_5 \cdot NH \cdot NH_2 + HNO_2 = C_6H_5 \cdot N_3 + 2H_2O.$$

Its production in this way gives the first indication of its properties, for unlike aniline and phenylhydrazine, which are bases, phenylazoimide is a neutral substance, resembling its haloid analogues, chlorobenzene, bromobenzene, and iodobenzene.

Although phenylazoimide was first brought to light by Griess in 1866, the subject of triazo-chemistry lay dormant until the discovery of hydrazoic acid by Curtius in 1890. Since that time the province has been a flourishing one, and the number of triazo-compounds which have been prepared and studied by Curtius and his pupils constitute an imposing section of nitrogen chemistry. It is principally with the acid azides, substances in which the triazo group plays the same part as chlorine in benzoyl chloride, that the investigations of Curtius have been concerned, and it is noteworthy that some of the earliest syntheses of polypeptides were effected by him simultaneously with Emil Fischer through the agency of these compounds; in the subsequent development of this field, however, the azide process gave way to the linking up by chlorides, as adopted and elaborated by Fischer. The method by which Curtius prepared his acid azides is really an adaptation of the change by which hydrazoic acid itself is obtainable from hydrazine, namely, by the action of nitrous acid upon the hydrazides of the respective acids, and it may be stated in general terms that any derivative of azoimide may be produced in this way provided the corresponding derivative of hydrazine is available; but this is the case only in certain classes of compounds, and the preparation of aromatic azoimides is best

accomplished by a process due to Noelting, which consists in adding sodium azide to the diazonium sulphate :

$$X \cdot N_2 \cdot HSO_4 + NaN_3 = X \cdot N_3 + N_2 + NaHSO_4.$$
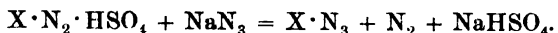
The remarkable instability of the diazonium azide, upon which this reaction depends, recalls that of the diazonium iodide, following which the iodine atom may be introduced into a benzenoid compound, and incidentally offers one more analogy between the triazo-group and a halogen. Moreover, resemblance to the haloid elements is suggested not only by this method of introducing an azoimide complex into the aromatic nucleus, but also by the circumstances attending its removal. It is well known that a chlorine atom in the benzene ring is so firmly attached that it cannot be removed by hot caustic alkalis, but that if nitro-groups also are present in the ortho- and para-positions, the halogen may be removed quite easily, so that picryl chloride is converted into picric acid by the action of water. Very similar relationships prevail among the substituted azoimides of benzene and naphthalene, from which hydrazoic acid may be eliminated according to well-defined principles.

It is now six years since we were led, at the Royal College of Science, to a study of the triazo-group by the accidental discovery of triazocamphor, a substance which displays properties in some respects novel, and in this connexion it gives me the greatest pleasure to acknowledge that the development of the subject has been in a large measure due to the courage and ingenuity displayed in its early stages by my former colleague, Dr. H. E. Fierz. The majority of the new materials differ from those of previous workers in belonging, not to the aromatic series, but to the other great class of organic substances, the aliphatic derivatives. It is with a study of the general behaviour of the triazo-group in the diverse environment afforded by these two classes that we have been concerned, and with this object have prepared azoimides of such simple types as acetalde-hyde, acetone, acetic acid, ethyl acetate, acetamide, ethyl alcohol, ethyl ether, substituted malonic acids, the unsaturated hydrocarbons ethy-lene and propylene, and, lastly, ethylamine. To these have been added certain bistriazo-compounds, namely, those of ethane, acetic ester, malonic ester and acetoacetic ester. In this latter class the explosive character of the triazo-group has been very prominent ; for instance, whilst a drop of ethyl triazoacetate when thrown on a hot plate merely inflames without detonation, 1 : 2-bistriazoethane explodes with considerable violence ; and this property is particularly notice-able when both triazo-groups are attached to the same atom of carbon, 1 : 1-bistriazoethane continuing in existence only a few minutes after isolation, when it disappeared with a deafening explosion. Another characteristic feature of these materials becomes evident when their vapour is inhaled, the experience of pleasure in an ethereal odour being quickly followed by a throbbing sensation at the base of the
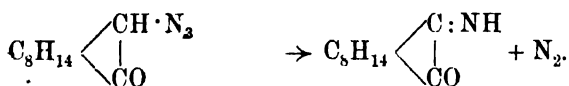
forehead often accompanied by palpitation of the heart. Whilst, however, the derivatives of benzene and naphthalene usually acquire an odour of anise by the introduction of the triazo-complex, the perfume connected with such substances as the azoimides of ethyl acetate, ethyl alcohol, acetone, ether and acetic acid, is quite devoid of the anise character, and is indeed much fainter than that of the parent compound in each case.

The method by which these aliphatic azoimides have been prepared is extremely simple. It depends on interaction of the corresponding halogen derivative with sodium azide ; for example,

$$CH_3 \cdot CO \cdot CH_2Cl + NaN_3 = CH_3 \cdot CO \cdot CH_2 \cdot N_3 + NaCl,$$
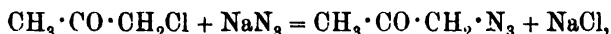
and appears to be almost general. The reaction has been lately applied to the nitrosochlorides of pinene, dipentene, the limonenes and terpineols, and it has been further found that the azoimide complex may be exchanged for the nitroxy-group in nitrosates, such as those of amylene and dipentene.

The various degrees of stability displayed by the azoimide nucleus is the feature which chiefly concerns chemists. Three principal types of decomposition may be recognized. The environment least conducive to stability betrays itself in the liberation of two nitrogen atoms in the elemental form, leaving the third atom attached to the carbon which originally carried all three. This is exhibited by triazoantipyrine, which loses nitrogen spontaneously at common temperatures, and passes into a bright red azo-compound. Triazoacetone undergoes this change more slowly, but may be stimulated into activity by the catalytic effect of alkali, a property which it shares with triazocamphor,

$$C_8H_{14} \Big\langle \begin{matrix} CH \cdot N_3 \\ | \\ CO \end{matrix} \qquad \rightarrow \ C_8H_{14} \Big\langle \begin{matrix} C:NH \\ | \\ CO \end{matrix} + N_2.$$

Sometimes excess of alkali must be used and the temperature raised, as in the case of triazoacetic acid, salts of which, when thrown into hot caustic potash, immediately begin to liberate two-thirds of their nitrogen as gas. The acid azides offer further illustrations of this decomposition, and here the phenomenon is accompanied by a remarkable atomic transformation, first brought to light by Curtius, later studied by Schroeter and others, the denuded nitrogen atom actually changing places with the carbon which formerly carried the triazo-group, with the result that *iso*cyanates are produced :
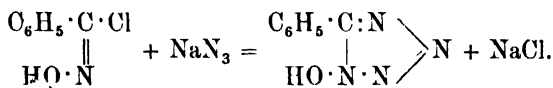
$$X \cdot CO \cdot N_3 \ \text{------} \!\!\longrightarrow X \cdot N : C : O + N_2.$$
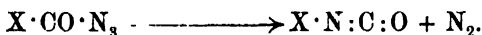
Sometimes this alteration is explosive, as in the case of triazoacetic azide, $N_3 \cdot CH_2 \cdot CO \cdot N_3$.

The next class of transformation undergone by the triazo-complex is more moderate. It was discovered by Dimroth, and may be described as an unfolding of the three-atom nitrogen ring without loss of the element, all three atoms of which remain in the form of a chain such as occurs in diazoaminobenzene ; triazen derivatives of this type are; in fact, easily obtainable by the action of alkyl magnesium halides upon organic azoimides,

$$C_6H_5 \cdot MgBr + C_6H_5 \cdot N_3 = C_6H_5 \cdot N : N \cdot N(MgBr) \cdot C_6H_5.$$
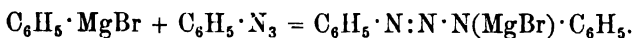
Although some external agency is usually necessary for this type of transformation we have found cases in which it takes place spontaneously. For example, allylazoimide, a colourless, mobile liquid when freshly prepared, rapidly changes into a white crystalline solid, consisting of a diazoamino-compound isomeric with the original material, whilst an attempt to prepare benzhydroximic azide led forthwith to its isomeric transformation product, hydroxyphenyltetrazole,

$$
\begin{array}{c}
C_6H_5 \cdot C \cdot Cl \\
\parallel \\
HO \cdot N
\end{array}
+ NaN_3 =
\begin{array}{c}
C_6H_5 \cdot C : N \\
| \quad\quad \Big\rangle N \\
HO \cdot N \cdot N
\end{array}
+ NaCl.
$$

More recently, the Italian chemists, Palazzo and Oliveri-Mandala, discovered that fulminic acid and methylcarbylamine, both highly unsaturated compounds, also are capable of producing this effect on the azoimide nucleus, converting hydrazoic acid into 1-hydroxytetrazole and 1-methyltetrazole respectively, whilst tetrazole itself is obtainable by the interaction of hydrazoic and prussic acids,

$$
HCN + HN_3 =
\begin{array}{c}
HC : N \\
| \quad\quad \Big\rangle N. \\
HN \cdot N
\end{array}
$$
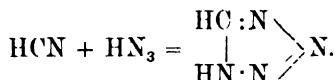
The third class of alteration undergone by the triazo-group involves its complete elimination from the molecule in combination with hydrogen, its place being taken by the hydroxy-group. The simplest illustration of this case followed attempts to prepare triazomethylamine, $N_3 \cdot CH_2 \cdot NH_2$, which we found could not be realised because derivatives of that substance display the remarkable property of liberating hydrazoic acid when treated with cold water. The same thing happens when triazotised carbon is associated with a halogen, triazoethylene dibromide, for example, yielding hydrazoic and hydrobromic acids after a few minutes contact with ice-cold water ; for this reason it was not possible to realise triazoacetylene, the copper derivative of which might be expected to excel that of acetylene itself in explosibility. More generally, however, this type of decomposition requires the action of alcoholic potash for its completion.

The behaviour of the triazo-group in respect of these three classes of transformation is controlled by its molecular environment, but all

organic azoimides have this in common, that they undergo change of
the first type—namely, loss of two-thirds the azidic nitrogen, when
treated with 80 per cent. sulphuric acid, or with various reducing
agents.   Moreover, they are all extremely sensitive to the action of
light.   As from time to time the marked analogy between the triazo-
complex and the halogens has been emphasized, it should be mentioned
that one complete contrast has lately been found.   The halogen
derivatives of ethylamine are known to part so readily with halogen
hydride, that chloroethylamine and bromoethylamine cannot be
liberated from their salts without immediately passing into di-
methyleneimine, $\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array}\Big\rangle NH$, isomeric with the unknown vinylamine
or aminoethylene.   Salts of β-triazoethylamine, on the other hand,
behave like salts of ethylamine itself, and so stable is the resulting
triazo-base that it may be distilled from solid potash under reduced
pressure without loss of hydrazoic acid.

Many disappointments have occurred in studying the triazo-
group, and the most conspicuous one which I have to admit is the
failure to produce hexatomic nitrogen ; in view of the resemblance
between the complex in question and the halogens, and the associa-
tion of two atoms of the latter in their free molecules, it was to be
expected that a new modification of nitrogen might arise by linking
together two triazo-radicles.   Experiments with this object have
failed, and if differently arranged efforts in the same direction are
also barren of result, the reluctance of the two nuclei to become
united may be regarded as having some bearing on the question of
the constitution and transformations of the triazo-group.   To aid in
the elucidation of this is, indeed, the principal purpose of the fore-
going observations, in view of our present ignorance regarding the
disposition in space of the atoms or groups which are associated with
nitrogen in its organic derivatives.   Such disposition or configura-
tion is fairly well understood with respect to carbon, the original
views of Kekulé, as developed by van 't Hoff, having stood the test
of forty years' unceasing experimentation, but the efforts of chemists
to fathom the nature of combined nitrogen, and the arrangements in
space of its varying valency directions, have not been so successful.
Nitrogen remains a Sphinx among the elements, propounding riddles
to the inquiring chemist, although happily, unlike her prototype, she
does not annihilate those who fail to solve them.

[M. O. F.]

Recent Experiments with Invisible Light.

BY far the greater proportion of the discoveries which have been
made in Natural Science up to the present time depend upon observa-
tions made with the eye, either with or without the aid of optical
instruments · ·The eye is, however, sensitive to only a very small
part of the total radiation which reaches it, and it seems not unlikely
that, if its range could be extended, many new phenomena would
immediately come to light. By the employment of photography and
of instruments which detect and measure the intensity of the infra-
red or heat rays, much new information has been gathered, especially
in the science of spectroscopy; but usually these methods have been
applied only in cases where the invisible radiations were known to be
present. It seemed quite probable that if photographic methods
were applied to various physical phenomena which excluded the
action of any but invisible rays, new facts would probably be dis-
covered. I can illustrate what I mean by taking two striking cases
which were found at the very outset of the investigation, and which
will be more fully discussed presently.

If the finger be dipped into powdered zinc oxide and rubbed
over a sheet of white paper, eye observation is absolutely unable
to detect the presence of the streaks made by the white powder,
unless it has been very thickly applied. If, however, we photo-
graph the paper with ultra-violet light, we obtain a picture in which
the streaks are as black as if made with powdered charcoal. This
suggests that if we apply the process to the photography of the moon
and planets, we have some reason to suspect that substances which
cannot be detected visually may come out in the photographs, a
surmise which has been justified in one case at least. This and
other similar cases will be taken up in detail presently.

As an illustration of how the method may be applied to the
investigation of various physical phenomena, we may take another
interesting case, in which a new radiant emission from the electric

spark has been discovered. It was suspected that the very short waves discovered by Schumann, which are powerfully absorbed by air, might possibly render the air fluorescent, the emitted light being invisible, however, on account of its short-wave-length. A heavy spark discharge was accordingly placed behind a small disc of metal, which cut off all the direct light, and the surrounding region photographed with a quartz lens, which is transparent to the ultra-violet rays. It was found that the air in the neighbourhood of the spark actually did give off actinic invisible rays, the photograph giving the impression of a luminous fog surrounding the metal disc.

I will now show you an experiment which illustrates that two objects which cannot be distinguished under ordinary illumination may appear quite different when the light which illuminates them is restricted to certain regions of the spectrum. I have here two pieces of scarlet silk which cannot be distinguished the one from the other in the light of the incandescent electric lamps which illuminate this room. I now extinguish the lamps and place the two pieces of silk under this Cooper-Hewitt mercury arc lamp, and as you see one of them still appears scarlet as before, while the other appears very dark blue, almost black, in fact. The peculiarity of the mercury lamp lies in the fact that it gives out little or no red light, consequently red objects in general appear almost black. The peculiarity of this particular piece of silk, by virtue of which it appears quite as red as in ordinary lights, lies in the fact that the red dye with which it is coloured is fluorescent under the action of the green rays from the lamp : the red light is manufactured, so to speak, from the green light by the colouring matter of the silk. If I place the arc lamp and the piece of silk behind this large sheet of red glass, you will observe that the fabric is actually brighter than the lamp itself, probably eight or ten times as bright. We can form an image of the lamp on the silk with a lens, and the image will be many times brighter than the lamp, which might be taken as a refutation of the old and well-known theorem in optics that no optical system can yield an image brighter than the source (!) Here is another piece of white silk upon which I have made some red spots with this same dye. By the ordinary illumination of the room it is seen to be white, with large pink polka dots, something quite suitable for a young lady's summer gown ! I now place it behind the red screen under the mercury arc and it at once becomes quite diabolical in appearance, bluish-black with flaming spots of scarlet, entirely unsuitable for the aforementioned purpose. The dye which was used for colouring these fluorescent fabrics was rhodamin. The conditions of illumination and observation are, of course, rather special in these cases, and I have introduced them merely to illustrate how the eye may be deceived under certain conditions.

Practically all sources of light in ordinary use give out more or less ultra-violet light which plays no part in vision, but which can be

rendered apparent in various ways. I have on the table a new arrangement by which these rays can be separated from the visible ones. The apparatus is practically identical with the device quite recently used by Professor Rubens and myself for isolating the longest heat waves that have been discovered up to the present time. It can be used as well for the isolation of the ultra-violet, since its action depends upon the high refractive index which quartz has for these two types of radiation. The source is, in this case, an electric spark contained in this box, and the ultra-violet rays are brought to a focus upon a small circular aperture in a cardboard screen. The focal length of the lens is so much greater for visible light that these rays do not come to a focus at all, but are spread over a circular area of a diameter nearly half that of the lens.

A penny has been fastened to the centre of the lens with wax, and this shields the aperture from the cone of visible rays coming from the central portions of the lens. If I hold a sheet of white paper above the aperture you observe that it remains dark, that is, no visible rays pass through to the paper; if, however, I substitute for the paper this mass of uranium nitrate crystals, the presence of the ultra-violet rays is made manifest, the crystals shining with a brilliant green light.

Certain vapours shine with a brilliant light when exposed to these invisible rays. One of the most striking is the vapour of metallic mercury, which I can show you by boiling the metal in this flask of fused quartz placed above the aperture. The metal is boiling now, and you can all see the brilliant cone of green light which marks the path of the ultra-violet rays through the metallic vapour. If I hold a thin sheet of glass between the aperture and the flask you will observe that the vapour instantly becomes dark, for the glass stops completely the rays in question.

The vapour of mercury exhibits an absorption band in the ultra-violet region which resembles the band at wave-length 5893 shown by dense sodium vapour. So powerful is this absorption that I have detected it in the vapour of mercury at room temperature. It occurred to me that this light instead of being absorbed might possibly be re-emitted by the vapour laterally in all directions. To test this point I sealed up a drop of mercury in an exhausted flask of quartz, and focused the light of the mercury arc (burning in a silica tube) at the centre of the bulb, which was not heated. The bulb was then photographed with a quartz lens, and the picture clearly showed the cone of focused rays precisely as if the bulb were filled with smoke. This is another very good example of how new discoveries may be made by ultra-violet photography.

If the object to be photographed gives off visible rays in addition to the invisible ones, it is necessary to remove these by a suitable screen or ray filter. We will begin by considering some remarkable effects which are obtained when sunlit landscapes are photographed
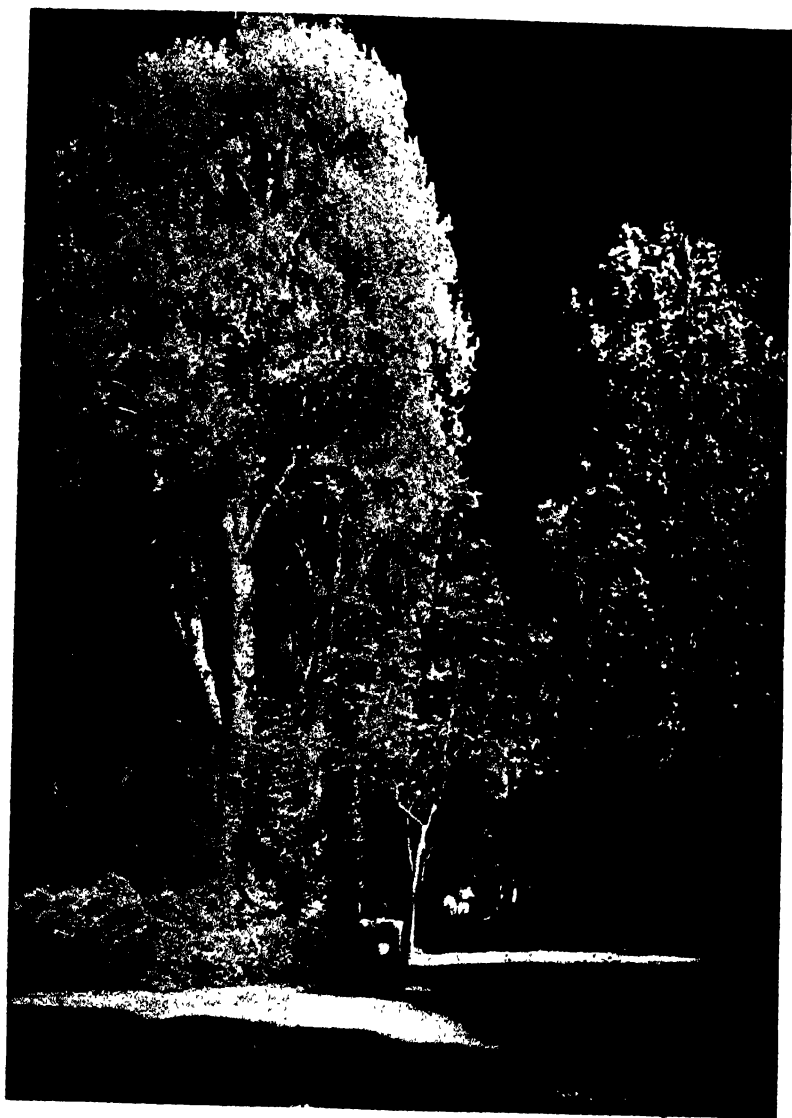
FIG. 1. PARK IN FLORENCE.

Photographed by infra-red rays.

FIG 2   QUARRY IN SYRACUSE

Photographed by infra-red rays

by means of the obscure rays at the extreme red end of the spectrum. A screen can be prepared which transmits these rays, and is at the same time opaque to all other radiations, by combining a sheet of the densest blue cobalt glass with a solution of bichromate of potash or some suitable orange dye.

Such a screen transmits a region of the spectrum comprised between wave-lengths 6900 and 7500. Though this region is visible to the eye if all other rays are cut off, it is so feeble in its action that it plays no part in ordinary vision, being overpowered by the other radiations. We may thence, for convenience, call photographs made through such a screen infra-red pictures, though the infra-red. region is usually considered as beginning at the point where all action upon the human retina ceases.

The photographs which I am now going to show you were taken through such a screen, with the spectrum plates made by Wratten and Wainwright. The time of exposure was about three minutes in full sunlight, with the lens stop set at $f/8$. The views were, for the most part, made in Sicily and Italy, and have a very curious appearance, for while the sky comes out in all of them almost as black as midnight, the foliage of the trees and the grass come out snow white. This peculiar effect results from the failure of the atmosphere to scatter these long rays. The green leaves, however, reflect them very powerfully, or more correctly, transmit them, since we are dealing with pigment or transmission colour. If we look at a landscape through the screen, carefully protecting the eye from all extraneous light with a black cloth, we shall find that the trees shine with a beautiful rich red light against a black sky. This condition obtains only on very clear days, for the presence of the least haze in the air enables it to scatter the long rays, and you will notice that in those pictures which show the sky down to the horizon, there is a progressive increase in its luminosity as we pass from the zenith downwards, as a result of the greater thickness of the mass of air sending the scattered rays to the camera.

Another point to be noticed is the intense blackness of the shadows in the infra-red pictures, due to the fact that most of the light comes directly from the sun and little or none from the sky, which reminds one forcibly of the conditions which obtain on the moon, where there is no atmosphere at all to form a luminous sky.

When we come to the subject of photographs made with ultra-violet light, we shall find that we have the conditions reversed, for practically all of these very short waves are scattered by the atmosphere, and we have no shadows even in full sunlight.

We will now run through the series of infra-red pictures as rapidly as possible, for I have a considerable number of them. The one which is on the screen is one of the finest in the collection (Fig. 1). It was made in the park at Florence, and shows the long drive, over-shadowed by trees, the one in the foreground being particularly fine

in appearance. The next one (Fig. 2) was made at the bottom of one of the old quarries or latomiæ at Syracuse, the view looking out through a cave-like formation at a group of almond trees, with which the quarry is overgrown.

Here is a fine row of cypresses growing by an old gate, taken on a somewhat hazy day, with the sky appearing a little lighter than usual. Some of the pictures show the advantage gained in bringing out the detail of distant objects seen through the atmospheric haze, and it does not seem impossible that photographs of the brighter planets made through an infra-red screen might prove interesting if the planets are surrounded by a light scattering atmosphere, for we must bear in mind that the surface of the earth, as seen from a neighbouring planet, would be seen through a luminous haze, equal in brilliance to the blue sky on a clear day—that is, it would present much the same appearance as is presented by the moon when seen at noon-day.

We will now look into the question of how things would appear if our eyes were sensitive only to ultra-violet light. In applying the same method which we have used for the infra-red, we require a screen which is opaque to all visible light, but which transmits the ultra-violet.

Glass is opaque to these rays, cutting them off almost completely, and for this reason we cannot employ glass lenses. Quartz, on the other hand, is exceedingly transparent to these invisible rays, but it is a little difficult to find a medium which is transparent to them and at the same time quite opaque to visible light. Indeed, there is only one substance known which completely fulfils such a condition, namely, metallic silver. If we deposit chemically a thin film of metallic silver on the surface of a quartz lens, a certain amount of ultra-violet radiation between 3000 and 3200 is able to struggle through and form an image on the plate.

I have used silver films through which the filament of a tungsten lamp is invisible. The best thickness is that at which the tungsten lamp is just barely discernible. If the objects to be photographed are illuminated with the light of an electric spark, or some other source rich in ultra-violet rays, much thinner films of silver can be employed, but in the case of sunlight, which has passed through the earth's atmosphere, the ultra-violet in the region for which silver has its lowest reflecting power and greatest transparency has been so tremendously weakened by atmospheric absorption, that it is necessary to employ thick films and long exposures, otherwise the action upon the photographic plate results chiefly from the violet and ultra-violet rays, which are capable of traversing glass.

As an illustration of the behaviour of silver films of different thicknesses, used as ray filters, we may take some pictures which were made for the purpose of studying the reflecting power of various metals, suitable for telescope mirrors, for ultra-violet photography.
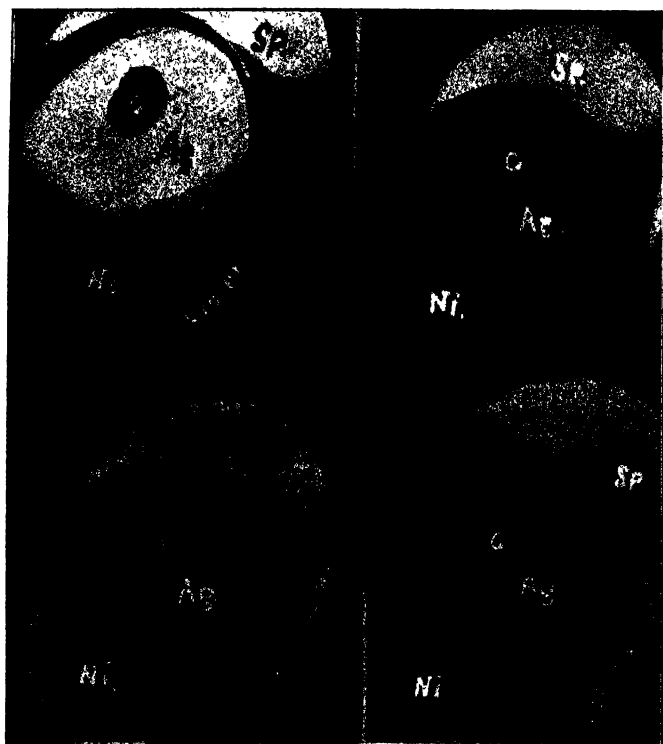
FIG. 3.

VISIBLE LIGHT.

ULTRA-VIOLET LIGHT.

FIG. 4.

As silver reflects only about 4 per cent. of the ultra-violet in the spectrum range for which it is transparent, a silvered glass reflecting telescope for this purpose is obviously out of the question. Speculum metal is fairly suitable, but speculum mirrors of large size are troublesome, and difficult to procure. I accordingly worked out a method of depositing nickel on glass. The glass is first silvered, and then electro-plated with nickel, by a process which I have described recently in the Astrophysical Journal (Dec. 1911). The double sulphate of nickel and ammonia is used with one or two dry cells. The solution must be very dilute (10 grams or less to the litre), otherwise the nickel strips the silver from the glass. We have here four pictures of a silvered glass dish, partially plated with nickel (Fig. 3). The silvered portion is marked Ag, the nickel Ni, while at G we have a spot of clear glass from which the metal has been removed. The dish stands against a flat plate of polished speculum metal Sp, and the metal surfaces reflect the light of the sky to the camera. The first picture was made by blue and violet light without any ray filter, and as you see the glass surface G is quite black, while the silver reflects much more powerfully than the nickel. The following three pictures were made with a quartz lens, coated with silver films of increasing thickness. The silver and nickel reflect to about the same degree in the second picture, in the third the silver is much darker than the nickel, while in the fourth the silver is seen to reflect no more than the spot of clear glass G. This last was made through a film, through which a tungsten lamp was invisible. If these ultra-violet rays were visible to us, metallic silver would appear to have about the same reflecting power and appearance as anthracite coal.

We will next take up the action of our atmosphere on these ultra-violet rays. I have taken two photographs of a man standing in the road in full sunshine, in the one case by ordinary light and in the other by ultra-violet radiation. In the latter the shadow is completely absent. Ultra-violet behaves in exactly the opposite way to the infra-red. The infra-red rays are enabled to drive through the atmosphere without being scattered laterally by the molecules of the air or the dust particles. The short or ultra-violet rays, on the other hand, are completely scattered, so that the greater part of the ultra-violet light which reaches the surface of the earth comes from the sky and not directly from the sun. If our eyes were sensitive only to ultra-violet we should find the world appearing not greatly different from the aspect which obtains at the time of light fog. We should, indeed, see the sun, but it would be very dull, and there would be no shadows, just as there are none on a foggy day. We should walk the earth like Peter Schlemeil, the shadowless man of the German fable.

The next picture (Fig. 4) illustrates the opacity of ordinary window-glass to ultra-violet radiation. It will be noticed that there is no trace of the landscape seen through the glass window, although it is clearly rendered in the companion picture taken with visible light. Another

difference to be noted in these pictures is that the flowers in the garden, which are white in the picture taken with visible light, disappear entirely in the picture taken by means of the ultra-violet radiation. · The white garden flowers become almost black as is shown in Fig. 5, which shows white phlox photographed by visible and ultra-violet light. It occurred to me that this ability of the white flowers to absorb the ultra-violet rays might play some economic part in the growth of the plant. I therefore experimented with some flowers which had been grown under glass, and had thus been deprived of ultra-violet, but I was unable to find any marked difference between those which had been grown in the open and others which had been deprived of their full quota of this radiation. It is possible that if the experiments were carried on through the course of a number of generations we should find a difference. I have found, however, that all white flowers are not equally dark when photographed with ultra-violet light. White geraniums, for example, come out much lighter than common white phlox, which is practically black when photographed through the silvered quartz lens.

In order to demonstrate the difference in the appearance of one of the common pigments when viewed respectively with visible light and with ultra-violet radiation, some letters were painted in Chinese white on a page of a magazine. In the photograph (Fig. 6) taken with visible light the Chinese white appears as white as the paper itself, if not indeed whiter ; but, photographed with the ultra-violet radiation, it comes out absolutely black. One may say that what is Chinese white in visible light becomes Japan black in ultra-violet. Under this radiation also black printer's ink becomes lighter than in visible light. This failure in the reflecting capacity of Chinese white is a source of some annoyance in reproducing drawings executed in part in this medium, as has been pointed out by Mr. A. J. Newton. In working with my Chinese white I made a mistake in one letter in the word "appears," and carefully wiped it out, leaving no trace of the correction discernible in visible light ; but when the photograph was made with the ultra-violet, the erasure, otherwise invisible, showed as a black smudge. The ultra-violet camera is evidently very much more sensitive than the eye to the presence of traces of Chinese white on the printed page, for so far as I could see every particle of the pigment had been removed. Whether this has any bearing upon the detection of forgeries has yet to be discovered.

Another class of work in which this comparative study is likely to be of service is the photography of celestial bodies. For the full moon the exposure through the silver screen was two minutes with ultra-violet light belonging to the region 3000 to 3200. This length of exposure necessitated an equatorial telescope with some means of driving it to compensate for the moon's movement. The support for my telescope was the framework of an old bicycle minus the wheels. This carried a 4-inch refractor and a quartz-silver telescope, and by the
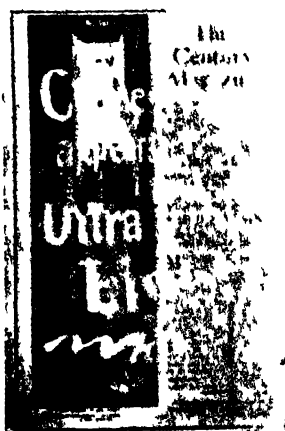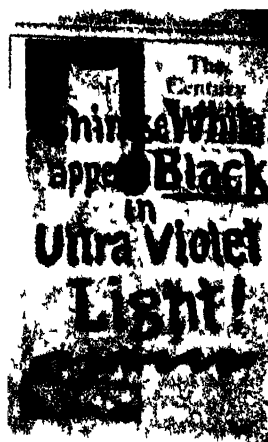
VISIBLE LIGHT
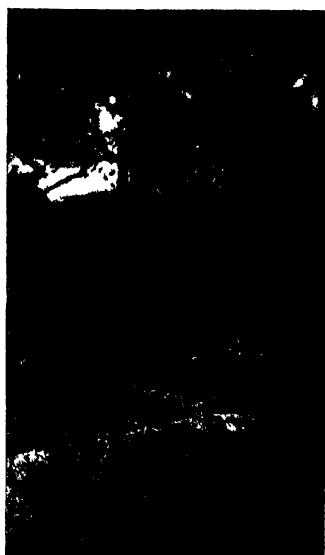
ULTRA VIOLET LIGHT

FIG

VISIBLE LIGHT

ULTRA VIOLET LIGHT

FIG 6

operation of a little screw it was possible to follow the moon accurately for half an hour. It will be seen at once (Fig. 7) that there is very little difference between the ordinary image of the moon and the one which is shown us by the ultra-violet radiation. Nevertheless, in the neighbourhood of Aristarchus, which is the brightest crater on the lunar surface, the photograph taken with the ultra-violet rays shows a dark patch which is absent on the one taken with visible light. I made an enlargement of the region in which this crater appears, and it is evident that there is in its neighbourhood a large deposit of some material which can only be brought out by means of the ultra-violet. These photographs of the moon make it appear extremely probable that by carrying on experiments of this nature on a larger scale we might get a good deal of new information as to the materials of which the moon is composed. It is possible to examine the igneous rocks of the earth under the different radiations, and then compare them with the pictures of celestial objects obtained at the same wave-lengths. I have found that some rocks, which when illuminated by ultra-violet rays appear darker than others, are lighter than the others in visible light.

Note added October 1911.

[I have had constructed a 16-inch mirror of 26-feet focus which I have coated with nickel, for extending the study of the ultra-violet photography of the moon and planets. This is now being used in combination with a plate of the new ultra-violet glass, 12 cm. square and 1 mm. thick, heavily silvered. The plate was made by Zeiss, and I find that it is quite as transparent as quartz for the rays transmitted by the silver filter. This reflector was mounted on the 23-inch equatorial of Princeton University, and some very fair pictures have been obtained, though the moon's motion in declination could not be followed with sufficient accuracy to secure the best results. Fig. 7 shows two views of the region around Aristarchus (indicated by an arrow), one made with yellow, the other with ultra-violet light. The dark deposit to the right of the bright crater comes out very clearly in the latter. The markings to the right of this region are quite different in the two pictures. Immediately below the pictures of the moon are three photographs made of two samples of volcanic "tuff" arranged one upon the other, with the crater Aristarchus marked with white chalk (as a check upon the exposure). The left-hand picture was made with yellow light, and the central specimen is lighter than the one surrounding it. The right-hand one was made with ultra-violet, and shows the central specimen distinctly darker. The middle picture was taken with violet light, which shows the two specimens of very nearly the same luminosity. I made an analysis of the fragment of tuff which

photographed dark in ultra-violet light, and found that it contained iron and traces of sulphur. Photographs of rocks stained with iron oxide did not show the required peculiarity, and I accordingly attributed the result to the sulphur. A light deposit of sulphur was formed on the surface of a piece of light-grey rock by directing a fine jet of sulphur vapour against it. The deposit was so slight that absolutely no trace of it could be detected by the eye. The specimen was then photographed with yellow, violet, and ultra-violet light, and it was found that the deposit was quite invisible in the first picture, faintly visible in the second, and quite black in the third—precisely the peculiarity shown by the deposit surrounding the crater Aristarchus. Fig. 8, *a*, *b*, *c*, show the gradual appearance of the deposit, which is an oval spot in the centre of the specimen. I feel inclined, therefore, to attribute this spot to an extensive deposit of sulphur, resulting from vapour ejected from the crater. The shape and vast extent of the deposit has always suggested to me that it resulted from material driven out in a volcanic blast.]

Returning now from the moon to the physical laboratory, we will consider a further phenomenon which has been discovered and studied by means of photography in the ultra-violet region. The vapour of mercury has an absorption-band in this region at wave-length 2536, which I have made the subject of a somewhat extended investigation. At low pressures the line is very narrow, resembling one of the D lines of sodium, and I have detected its presence in mercury vapour at room temperature, by employing a tube 3 metres long closed with quartz plates. It occurred to me that this vapour might prove to be the substance which I have long sought for the study of what I have named resonance radiation, i.e. a re-emission of light by absorbing molecules, of precisely the same wave-length as that of the light absorbed. Sodium vapour was found to exhibit the phenomenon, but the experimental difficulties were so great that very little was accomplished. A small box was made of brass and square plates of quartz. The inside was varnished and blackened with soot, a drop of mercury introduced and the box exhausted. The camera with its quartz objective was now trained on the box, and a beam of light from a mercury lamp (quartz) focused at the centre of the box. Though the eye could see no trace of the cone of rays, the photograph brought it out as distinctly as if the box was full of smoke. An exposure of only one second was necessary, and with a ten-second exposure the spectrum of the light scattered by the vapour was secured. It was found to consist of a single line only (the 2536 line), though the light entering the box was the total radiation of the mercury arc, the spectrum of which contained hundreds of lines. The pressure of the mercury vapour was about 0·001 mm., in other words, $\frac{1}{760000}$ of the pressure of the air in the room. It seems most extraordinary that a vapour at such a very low pressure and at the temperature of the room should glow so brilliantly with invisible light. A little further experiment-
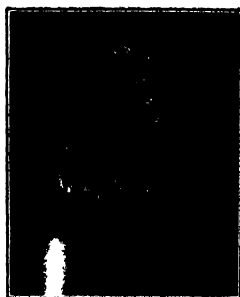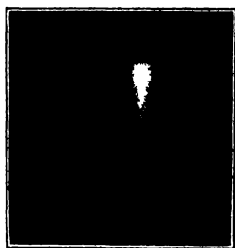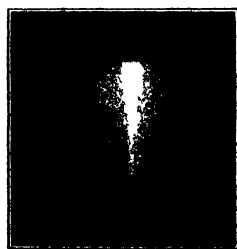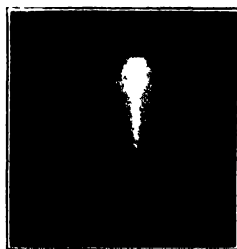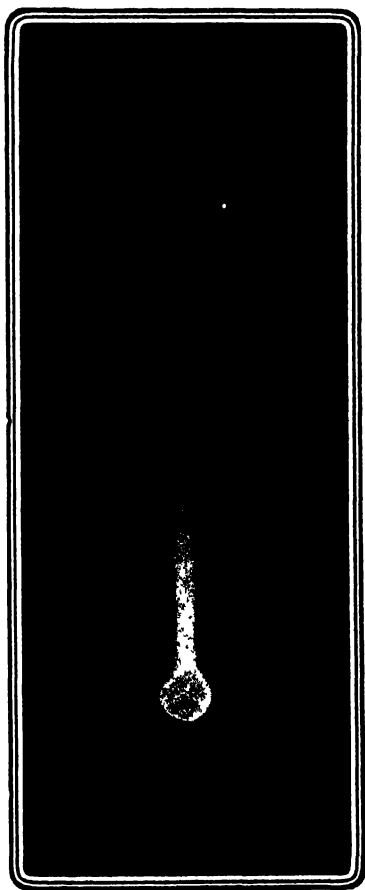
Fig 7
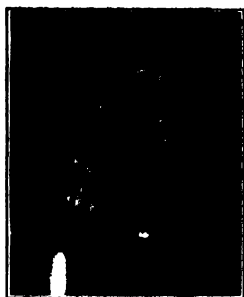
FIG. 8.

ing resulted in a further discovery. It was found that if the box was filled with air at atmospheric pressure, the cone of rays glowed feebly in the mercury vapour with which the air was saturated. As the pressure was reduced the glow increased in brilliancy, reaching its maximum at a pressure of about 5 mm. As the exhaustion was pushed further the mercury vapour outside of the cone became luminous, and at the highest vacuum attainable the glow filled the entire box. This is secondary resonance radiation excited by the primary radiation of the mercury vapour, which is excited by the cone of focused rays. The brilliancy of the cone remained about the same, so that we cannot attribute the bursting out of this secondary fluorescence to a mere increase in the brilliancy of the directly excited vapour.

Experiments are now in progress to determine why the presence of a few millimetres of air destroys all trace of the secondary radiation. Photographs of the glowing vapour in air at pressures of 5 mm., 1 mm., and 0 are reproduced in Fig. 8, d, e, f.

If we put the drop of mercury in a small flask with very thick walls, exhaust the air, and seal the neck of the flask with the oxy-hydrogen flame, we are in a position to study this interesting type of radiation in mercury vapour at high pressures. I found that as the temperature of the flask was raised the radiation came from a region nearer and nearer the front surface which was illuminated by the rays from the lamp, and that when the pressure was about ten atmospheres the ray from the lamp, which had a wave-length of 2536, was selectively reflected from the surface of the vapour, precisely as if the inner surface of the bulb were plated with silver. The other rays passed through the bulb with their usual facility. I am at the present time engaged in the study of just how the change from the resonance radiation (which is scattered in all directions) to the regular reflection takes place, a matter of great interest in connection with the theory of absorption and reflection. As a matter of fact, I expect it to turn out that the mercury light does not absorb the light at all, for experiments indicate that the lateral emission of the ultra-violet light is about as bright as when white paper is used to scatter the light.

Another interesting line of investigation which I have recently carried out illustrates how new discoveries may be made by the aid of ultra-violet photography. It occurred to me that the air surrounding an electric spark might possibly be rendered fluorescent by the absorption of the very short ultra-violet waves discovered by Schumann, but that the fluorescence might be made up wholly of ultra-violet light, and consequently invisible. I therefore photographed the region surrounding a powerful spark discharge with a quartz lens, shielded from the direct light of the spark by a circular disc. The photograph, when developed, showed a highly luminous aureole surrounding the spark and extending out in all directions to

a distance of nearly 2 cm. It was now necessary to prove that this was not light scattered by the dust particles in the air. To do this we have only to photograph the spectrum of the aureole. If it is similar to the spectrum of the spark, we are safe in attributing it to scattered light. If it differs we know that it must be fluorescence, or the genesis of waves of different wave-length from any present in the light of the spark. A photograph of the region surrounding the spark was made with a quartz spectrograph, and it was at once found that the spectrum was wholly different from that of the spark—in fact it was almost identical with that of the oxy-hydrogen flame. For the further study of the phenomenon, a piece of apparatus was devised by which the light of the spark could be more effectually shut off. A small hole was bored through a plate of aluminium fastened to the end of a short vertical brass tube. This plate formed one electrode, the spark passing between an aluminium rod lying along the axis of the tube and the under side of the plate at the point perforated by the hole.

In a perfectly dark room, if the eye was held a little below the plane of the plate, no luminosity could be seen in the air above the hole, if it was reasonably free from dust, yet a photograph taken with a quartz lens showed a bright beam, or squirt, of light issuing from the hole. A photograph of the phenomenon is here shown, and you will notice the strong resemblance which it bears to a comet. (Fig. 8, g).

Many weeks have been spent in an attempt to determine the exact origin of this radiation, and the question has proved to be the most baffling one which I have ever attempted to solve. The work is still in progress, and many remarkable observations have been made, each one leaving us more in the dark than before. As an illustration I may mention a circumstance discovered by Dr. Hemsalech and myself last winter in Paris. We found that if a jet of air was blown through the squirt of light the luminosity was destroyed in the region traversed by the moving current of air, but was of undiminished intensity both above and below this region. This makes it seem as if the emanation which comes from the spark, and which causes the luminosity of the air, must act for a brief time upon the air in order to cause the luminosity. It also shows that the emanation, whatever may be its nature, is not swept aside by the air current. We have also found that other gases become luminous when subjected to the spark emanations, the spectrum in each case being different and peculiar to the gas used, electrolytic hydrogen, for example, giving a strong luminosity.

It is thus apparent that by employing this " photographic eye " of quartz many new phenomena may be brought to light which have previously hidden themselves behind the limitations of the human eye. A study of the absorption by the candle-flame of ultra-violet has also been made. In this case the light emitted by the candle falls out of the problem, for its flame emits little or no ultra-violet.

I can show you a photograph of the shadow cast by a flame of this description, and you will observe that the shadow is blackest at the point where the flame is brightest, that is, at the point where the minute carbon particles, which, by their incandescence, cause the luminosity, are being set free from the hydrocarbon vapour.

There are other questions which can doubtless be investigated to advantage by means of ultra-violet photography. It is well known, for example, that the amount of ultra-violet light emitted by a body increases with the temperature. By photographing groups of stars through the quartz silver filter, and comparing the photometric intensities of the images obtained in this way with the intensities as shown on a plate made by means of yellow light, valuable data might be obtained. This method is merely an extension of one already in use at the Harvard Observatory.

[R. W. W.]

Friday, January 19, 1912.

His Grace the Duke of Northumberland, K.G. P.C.
D.C.L. LL.D. F.R.S., President, in the Chair.

Professor Sir James Dewar, M.A. LL.D. D.Sc. F.R.S. M.R.I.
Fullerian Professor of Chemistry, R.I.

Heat Problems.

[ABSTRACT.]

The approach to the absolute zero has rendered the problem of the determination of extremely low temperatures a very-important one. Within certain limits resistance thermometers or thermo-couples give satisfactorr results ; but now that a temperature within 3° of the absolute zero has been attained, other methods must be resorted to, and the only reliable one is by the measurement of changes at constant volume due to temperature in the pressure of a gas under less than one-third of an atmosphere. The limits of temperature measurable by this method vary with different gases ; helium, for example, giving accurate records to within 3° of the absolute zero.

Gas Thermometers.

A gas thermometer for lecture illustration is shown in Fig. 1. A is a copper sphere of a capacity of about 100 c.c., filled with pure hydrogen at a pressure of 273 mm., while immersed in melting ice. The free space, which is the volume of the uncooled narrow tubes required for connection to the manometer, is in this case so small that it may be neglected. A is placed in a metallic vacuum vessel B, containing liquid oxygen, and connected by a thick-walled narrow lead tube to a mercury manometer C. The apparatus is mounted on a movable frame D, so that the height can be adjusted for projection of the mercury levels. The change of pressure due to cooling the hydrogen in A is shown by the alteration in the levels of the mercury in the manometer. Liquid oxygen reduces the pressure to 90 mm., corresponding to 90° Abs., and if the liquid is exhausted through E, a pressure of 65 mm. is obtained ; i.e. the temperature of the sphere is now 65° Abs., because with this sphere filled as described the difference of mercury-levels in millimetres is practically equal to the temperature of the sphere in degrees absolute.
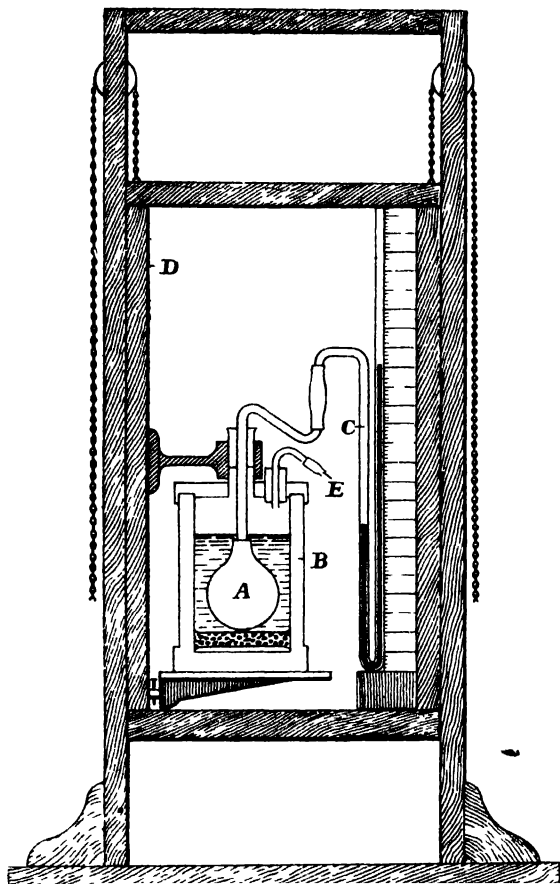
FIG. 1.

The following table gives the practical limits of gas thermometers filled with different gases at various initial pressures.

TABLE I.—PRACTICAL LIMITS OF GAS-THERMOMETERS.

Gas	Initial Pressure at 0 Deg. Cent. Millimetres of Hg.	Limit of Temperature to which Applicable. Deg. A.
CO_2	$\frac{1}{2} \times 273$	171·4
O	$\frac{1}{2} \times 273$	69·2
H	$\frac{1}{2} \times 273$	11·72
H	$\frac{1}{10} \times 273$	10·40
Helium	38×273	2·95
Helium	$\frac{1}{2} \times 273$	1·91
Helium	$\frac{1}{10} \times 273$	1·71

The lowest temperatures which can be attained with various cooling agents are of considerable interest. Gay Lussac showed that it was possible to freeze mercury by the evaporation of ice, and the experiment, arranged for projection on a screen, can be performed in the following manner (Fig. 2). A flat glass bulb, A, contain-
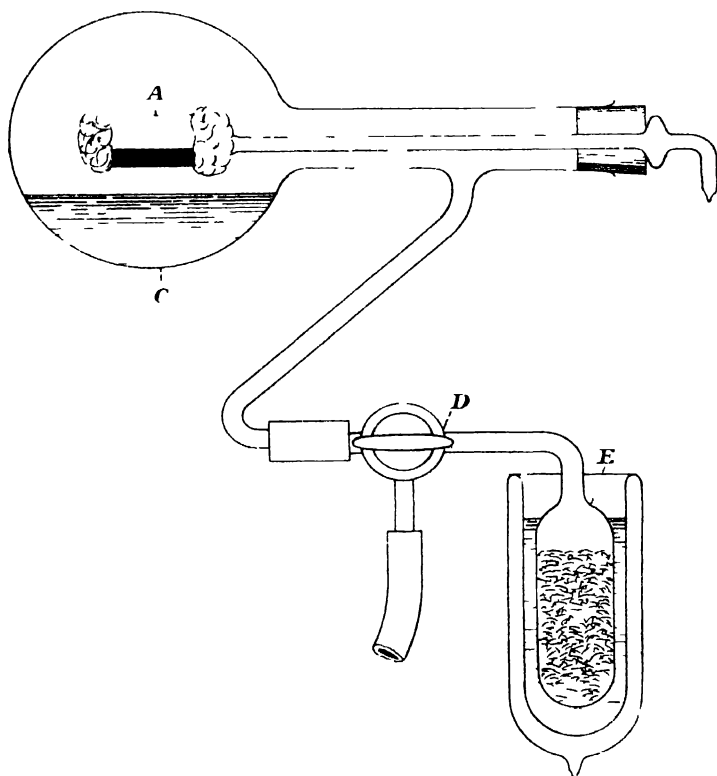

FIG. 2

ing the mercury, is supported on a quill tube in the flask C, containing sulphuric acid. This vessel is connected through a side tube in the neck by means of a 3-way cock D to an exhaust pump, and a bulb of charcoal E. At each end of A some strands of wet cotton wool are fastened. The charcoal having been cooled in liquid air, the exhaust pump is turned on to C for a short time; and the

charcoal is then brought into play by a quarter turn of D. The consequent reduction of pressure on the ice in the cotton wool on A, and therefore of its temperature, is such that in two minutes the mercury at each end of the tube freezes, the centre portion remaining liquid ; in four minutes the mercury becomes solid, which may be seen when the bulb is rotated. By this method a temperature of $-70°$ C. can be reached. Experiments made with various bodies as cooling agents give the following limits of temperature :—

TABLE II.—LIMITS OF TEMPERATURE ATTAINABLE WITH VARIOUS COOLING AGENTS.

Solid	Absolute Temperature attainable. Deg.	Pressure in mm. of Hg.	Fraction of T_c
Ice	203	0·001	0·32
CO_2 . . .	132	0 63	0 43
O	51	0 19	0 33
N	37	0 7	0 30
H	9	0 59	0 29
Helium . .	1·8	0 26	0 33
"X" . . .	0 4	—	—

In this table X is a hypothetical body as volatile compared to helium, as helium is to hydrogen. With the aid of such a substance it may be inferred that a temperature of within $\frac{1}{2}°$ of the absolute zero
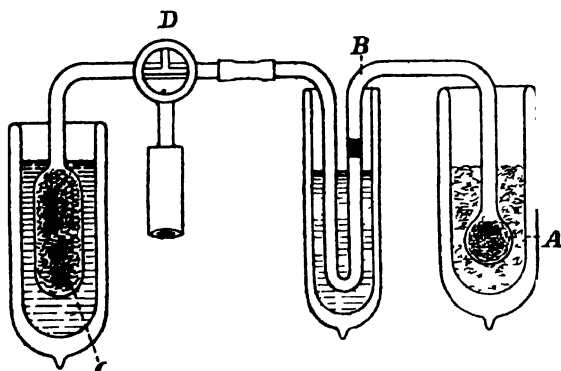

FIG. 3.

should be reached., It will be seen from the table that the temperature attained was almost invariably the same fraction of the critical temperature of the body, a fact which further emphasizes the

importance of the critical point. Other relations between the properties of a body and its critical constants are of interest, and are given in the following table :—

TABLE III.—CORRESPONDING TEMPERATURE RELATIONS.

Liquid coefficient of expansion varies as	$1/T_c$
Liquid coefficient of compressibility varies as	$1/P_c$
Liquid internal latent heat varies as	T_c
Capillary constant varies as .	P_c
Gas inversion point varies as .	T_c
Volume of gas molecule varies as	T_c/P_c
Maximum density varies as density at	T_c

The vaporization of ice at $-78°$ C. can be demonstrated by the apparatus shown in Fig. 3. A is a small bulb packed in solid CO_2, filled with ice in the form of frozen water-saturated cotton wool, which gives a large surface. This vessel is connected to the U-tube B immersed in liquid air. The tube and the bulb are highly exhausted by an air pump connected at the 3-way cock D, and then by charcoal C cooled in liquid air. The deposit is first seen in the form of a ring in the limb of the U-tube nearest the bulb A. Vaporization is very slow, and takes almost an hour before the deposit is sufficient to be easily visible.

With gas thermometers working under small gas pressure reliable results can be obtained, provided the differences in the height of the mercury columns are read by means of a cathetometer, and proper precautions taken in filling with the gas. A simple form of gas thermometer with the volume of the bulb as small as 5 or 6 c.c. is shown in Fig. 4. In small apparatus, where a more bulky instrument could not be used, this form works in a satisfactory way, giving readings within $0·5°$. when filled with helium or hydrogen under an initial pressure of 273 mm. at the melting-point of ice. The following diagram (Fig. 5) shows the type of the graphical curves given by such thermometers ; exhibiting a slight deviation from the theoretical straight line connecting absolute temperature and pressure. The various substances used in the calibration of such thermometers are marked on the curves. The deviations from the theoretical line are much exaggerated in the diagram. They are due to the variation in the
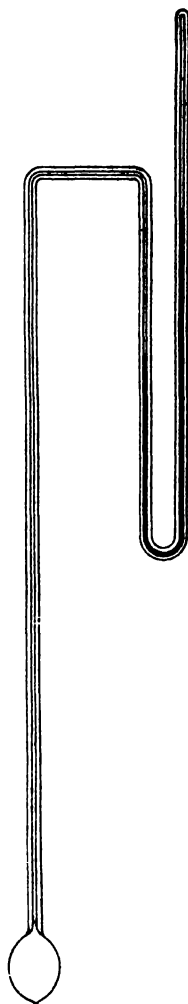
FIG. 4.

volume of the free space in different thermometers. Thus, if P and p are pressure readings of the manometer at T° and 275° Abs. respectively, then $T° = 273 \dfrac{P}{p} - \dfrac{P(p - P)}{c}$ where c is a constant
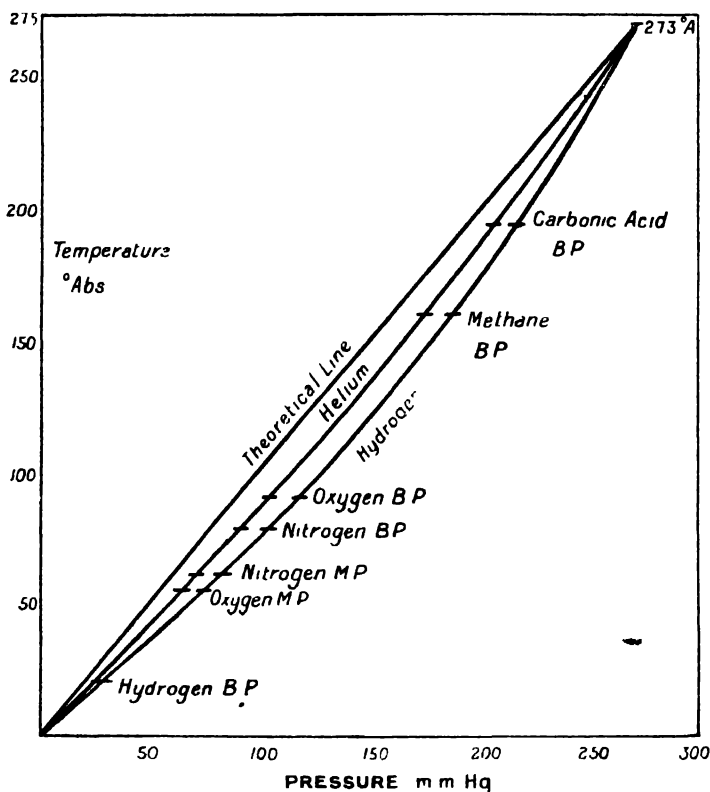

FIG 5

varying inversely as the ratio of the volume of the capillary to that of the bulb of the thermometer. Helium under a pressure of 273 mm. may be regarded as reliable as low as 3° Abs. If the pressure be reduced to 27·3 mm. at 273°, the limit of temperature is about 1°·7

INSULATION BY POWDERS.

In all low temperature work heat isolation is of the utmost importance. The double-walled glass vacuum flasks now so generally used for this purpose were first exhibited on this Lecture Table nineteen years ago. The efficiency of these vessels is much

inci eased by silvering the inner wall to form a reflecting sur-
face. Experiments made by filling the annular space with powdered
charcoal or silica showed that while with some flasks the loss of
heat could be reduced to about one-third, as a rule the results
obtained were not better than with the use of the silvered vessels.
This may be shown by the following experiment (Fig. 6). Three
vacuum vessels, A, B, C, containing liquid air, are sealed to a common
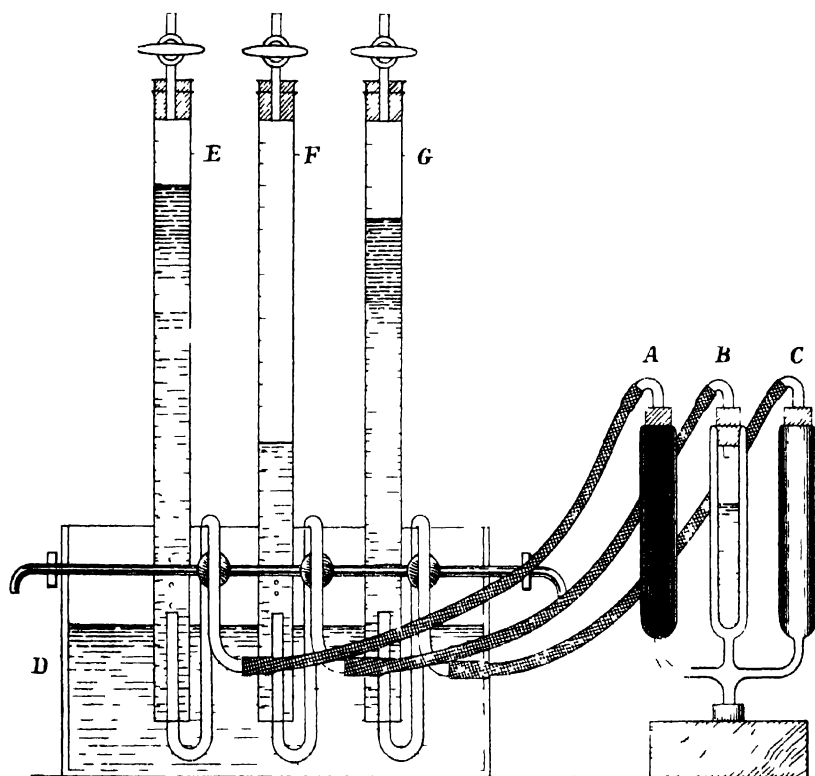
Fig. 6

exhaust. B is of the ordinary unsilvered variety; A and C con-
tain powdered charcoal and silica respectively in the annular space.
The three tubes are fitted with glass delivery-tubes leading through
rubber corks to a glass tank D filled with coloured water, con-
taining three uniform collecting-tubes, E, F, G. The evaporated
air from A, B, C is delivered simultaneously into these collecting-
tubes. In about five seconds F, connected with the plain tube B,

is almost full of air.   The rate of evaporation from the three tubes may be judged by the relative volumes of air in E, F, G, the proportion found being about 2 : 10 : 3.   While the manufacture of vacuum vessels is restricted to glass, probably no increased efficiency will be obtained by the use of powders as isolating agents, but if such flasks were made of fused silica the method might have considerable advantages.   Silica flasks would withstand very high temperatures, which would, however, render the use of silver as a reflecting surface an impossibility ; although nickel might be used.   If such a flask could be made quite impervious to gases, which is extremely doubtful, it would be especially suitable for the isolation of red hot bodies.

LIQUID AIR AND HYDROGEN DROPS.

In a Friday Evening Discourse on " Liquid Hydrogen Calorimetry," * the mode of manipulation of liquid gases for calorimetrical
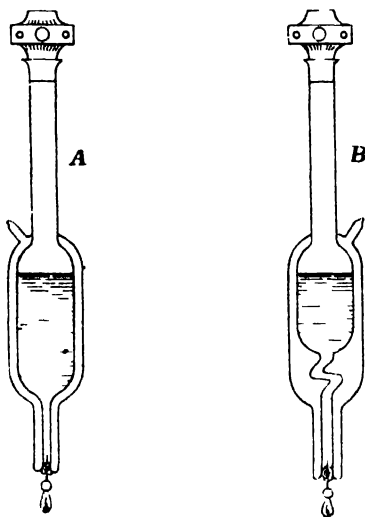

FIG. 7.

A shows the simple construction which can be used with the instrument made in quartz; if glass is used as in B, then a spiral has to be sealed in the exit tube, to take up the contraction caused by cooling to low temperatures.

experiments was discussed.   One fact which renders this simple method of calorimetry more difficult than it appears is the mobility

of liquid air, and more especially of liquid hydrogen. When any solid is dropped into such calorimeters violent ebullition ensues, and either can be carried over with the evaporating gas, in the form of fine drops or spray, into the collecting jar, and so falsify the results. The possibility of this can be proved by showing that drops of liquid air will retain their state through a fall of from 30 ft. to 100 ft. in air. To illustrate this, special dropping pipettes were supported from the ceiling of the Lecture Room. The construction of the nozzle is shown

A   B
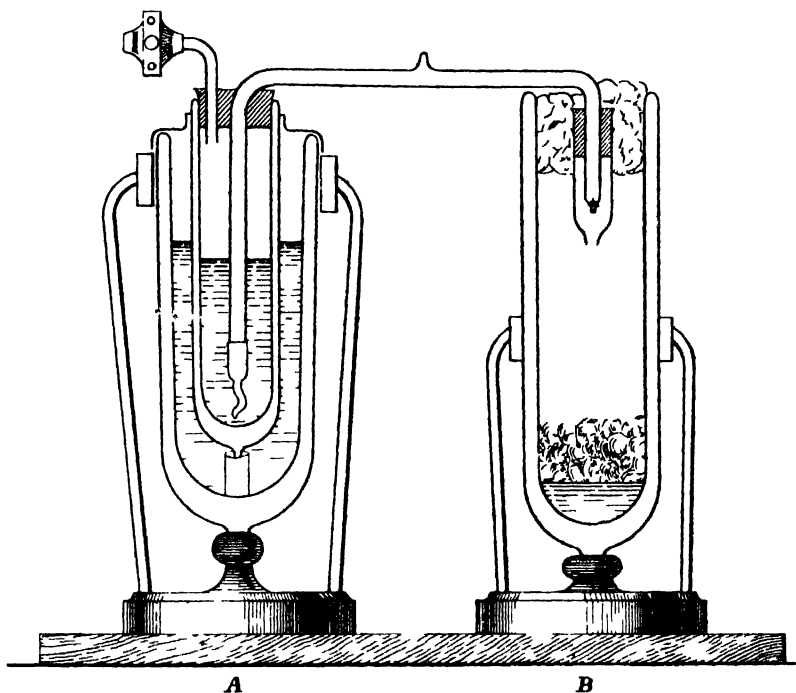
FIG. 8

in Fig. 7 ; it is filled with a wad of tightly packed cotton-wool, pierced with a coarse needle. By exercising a slight pressure on the liquid air above—a screw clip on a short length of rubber tube serves for this—the rate of dropping is easily regulated. Larger drops are obtained when a pin with a round glass head replaces the needle. The drops fall on a wet blackened board, and the impact is plainly audible and made visible by the surface of the board being obscured by a white mist as the drops rapidly evaporate. Such drops pass through a soap-bubble without bursting it. Hydrogen is remarkable in this respect, as the surface tension of liquid hydrogen is only

one-seventh that of liquid air, and its density one-fifteenth, while its temperature is only 20° Abs., i.e. one-fourth that of liquid air ; still, small drops of the liquid are easily traceable through a fall of 8 feet, by the trail of frozen air caused by their passage. The forma-tion of the liquid hydrogen drops requires a special form of silvered glass siphon (Fig. 8, A). The siphon is connected to a large silvered vacuum vessel containing the liquid hydrogen, fitted with a screw-cock for regulating the pressure, which controls the rate of dropping. The nozzle contains a loosely packed wad of wool, and to prevent fouling by condensation of air, it is surrounded by a piece of glass tube 4 inches long and $1\frac{1}{2}$ inch in diameter, drawn out below to $\frac{1}{2}$ inch, thus preserving an atmosphere of hydrogen about the nozzle. When the drops of liquid hydrogen are started, a succes-sion of tiny vortex rings of frozen air are visible from the nozzle to the floor as they fall gently through the air. If the siphon be fitted to a vacuum vessel about 18 inches long (Fig. 8, B), so that the drops can fall on some liquid air previously placed in the vessel, a cloud of solid air quickly rises from the surface, rapidly settling again when the drops are shut off. If a slow rate of dropping is maintained, the liquid hydrogen drops are easily seen, producing little jets of con-densed vapour as they dart rapidly about in the spheroidal state on the surface of the liquid air.

LIQUID AIR CALORIMETER.

Vacuum jacketed vessels have led to the construction of a simple form of gas calorimeter for the measurement of specific heats. The lecture form of the apparatus (Fig. 9) consists of a silvered vacuum vessel A containing liquid oxygen, fitted with an air-tight cap ; a small delivery-tube B leads to an inverted gas jar C. The cap has a central vertical tube closed by a rubber cork D. A is supported in a metal vacuum pot E containing liquid air. An aluminium cup F rests on asbestos wool in the bottom of A. Normally there is no evaporation from A, but if a fragment of the substance of which it is desired to ascertain the specific heat, is dropped into F by momentarily removing D, a quantity of liquid oxygen is evaporated as gas, collected in C, and the amount measured, from which the specific heat of the body can be calculated. A sphere of lead, of weight proportional to its atomic weight, is taken as a standard, this element maintaining a nearly constant atomic heat, following the law of Dulong and Petit, for a considerable range of temperature. Pieces of carbon, aluminium, copper and bismuth, in atomic propor-tion to the lead sphere, all liberate smaller quantities of gas, especi-ally carbon, where the value is found to be much below the average.

In all instances, however, the atomic heats of the elements fall below the normal value as the absolute zero is approached.

The mean specific heats of a few substances, for temperatures
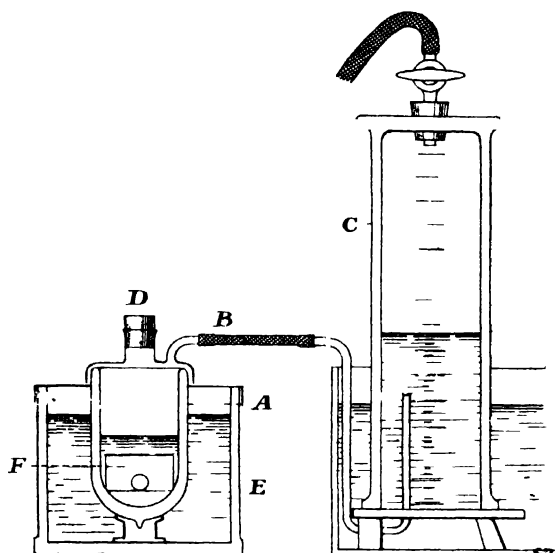
FIG 9.

ranging from 20° to 80° Abs., made with the liquid hydrogen calorimeter, are given in the following table :—

TABLE IV —MEAN ATOMIC SPECIFIC HEATS BETWEEN 20 DEG. AND 80 DEG. ABSOLUTE.

Diamond	. .	0·05
Graphite	.	0·17
Magnesium	.	1·71
Aluminium	.	1·12
Ice (molecule)	.	1·94

At the mean temperature of 50° Abs. it will be seen that the diamond has a very small specific heat, and all the other bodies in Table IV show a considerable decrease as compared with determinations made at ordinary temperatures. The theoretical curve of the change of atomic specific heat due to temperature on Einstein's theory,

is shown (Fig. 10). The problem of specific heats has been exten-
sively studied by Nernst, who has shown that they would probably
disappear before the absolute zero is reached. This result has given
rise to various theoretical speculations as to its cause, and in all
probability the solution will be found in the development of the
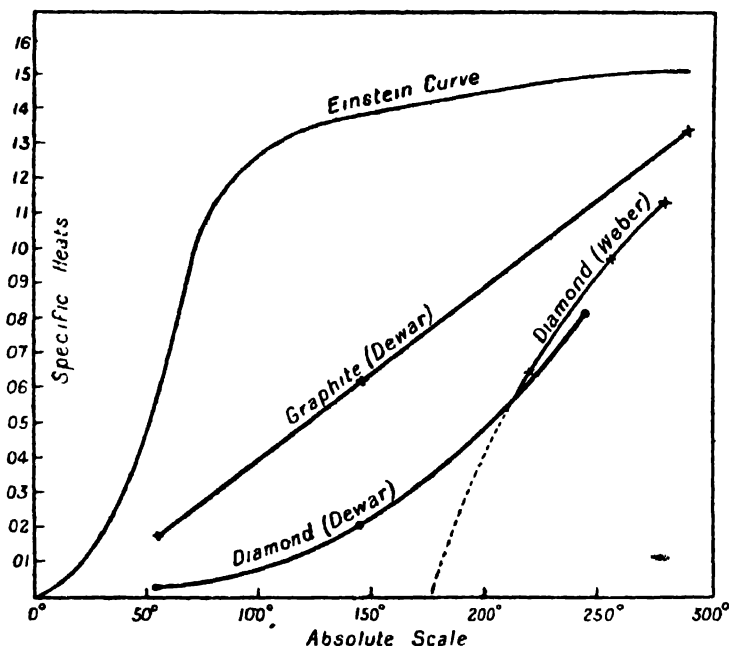electron theory. At the temperature of boiling helium Kamerlingh

FIG. 10.

Onnes has found that the electrical resistance of gold, mercury,
and platinum vanish. Thus, pure metals lose both specific heat
and electrical resistance below $4°$ Abs., suggesting that in this as yet
unexplored region existing theories fail. The properties of matter
at the absolute zero remains a purely speculative problem.

[J. D.]

Friday, February 9, 1912.

SIR WILLIAM CROOKES, O.M. LL.D. D.Sc. F.R.S., Honorary
Secretary and Vice-President, in the Chair.

JOHN ALLEN HARKER, ESQ.. D.Sc. F.R.S.

Very High Temperatures.

[ABRIDGED.]

EXACTLY a century ago this month Michael Faraday entered the
Royal Institution for the first time. He was then a youth of twenty,
in the last year of his apprenticeship to a bookbinder in Blandford
Street. Among the meagre records we possess of Faraday's early
life we find the following :—

"I had the good fortune, through the kindness of Mr. Dance,
who was a customer in my master's shop and also a member of the
Royal Institution, to hear four of the last lectures of Sir Humphry
Davy in that locality. The dates of these lectures were Feb. 29,
March 14, April 8 and 10, 1812." It was Faraday's habit to occupy
the seat in the gallery over the clock. He made very full notes of
the lectures, and afterwards wrote them up, indexed and bound them
with his own hands into a volume of 300 pages, which is now pre-
served at the Royal Institution.

Some months later Faraday writes : "Under the encouragement
of Mr. Dance I wrote to Sir Humphry Davy, sending, as a proof of
my earnestness, the notes I had taken of his last four lectures. The
reply was immediate, kind and favourable."

In March 1813, apparently largely on the strength of the impres-
sion made upon Davy by this volume of notes, Faraday was engaged
as assistant in the laboratory of the Royal Institution at a salary of
25s. a week, with two rooms at the top of the house.

The first lecture of Davy's course referred to was on "Radiant
Matter," and dealt, among other things, with the action of electric
sparks on gases. Ever since Volta's discovery in 1800 Davy had
been occupied with the study of the pile and the effect of the new
currents in producing heat and chemical change, thus leading up to
his decomposition of the fixed alkalis and the isolation of potassium
in 1807.

Following on this discovery, Davy proposed that a fund "should
be raised by subscription for the construction of a large and powerful
battery, worthy of a national establishment, and capable of promoting
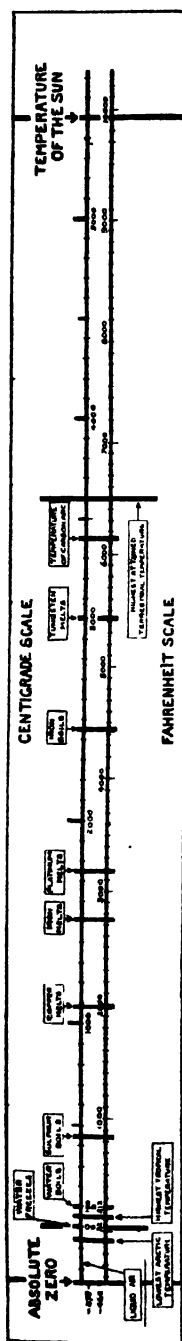
the great objects of science, and that this battery be erected in the laboratory of the Royal Institution." The sum required, a little over £500, was soon got together, and at the concluding lecture of the 1812 season the battery was put in action for the first time. We read in Davy's "Elements of Chemical Philosophy," iv. p. 110, an account of how he applied the battery to the running of an electric "arch" between two carbon rods. Parts of Davy's battery are still preserved at the Royal Institution.

I begin my lecture thus, merely to emphasize once more the truth of the adage of 3000 years ago : " There is no new thing under the sun."

In 1912, when considering the subject of "very high temperatures," we can claim, comparatively speaking, to be capable of little more than Davy accomplished a century ago. In his arc he melted all the most infusible materials known to him, including lime and magnesia, which are among the most refractory materials in use at the present day.

Turning now from the historic to the present aspect of our subject, permit me to begin with a few elementary considerations as to our conception of temperature. I think I am correct in saying that everyone has some idea in his own mind of a temperature-scale, a kind of intuition which is generally a fairly useful one for practical purposes. Probably I am not exaggerating when I say that even men of science, who always think for their professional purposes on the Centigrade scale, find themselves obliged to convert to Fahrenheit for an idea of the temperature of a room or of a summer's day.

I have endeavoured to give a graphic representation (Fig. 1) of the temperature scale as we know it, both in Centigrade and Fahrenheit degrees. You will notice the smallness of the interval between the extreme temperatures that prevail in the arctics and the tropics ; and how restricted the " cold " region down to absolute zero is compared with the possibilities in the other direction. While, on the one hand, Kammerlingh Onnes by the evaporation of

liquid helium under low pressure has succeeded in getting during the last few weeks to within $1 \cdot 1°$ C. of absolute zero, the highest recorded terrestrial temperature—that of an electric arc under high pressure—falls short of the sun's estimated temperature by some 2000° C.

Some landmarks in our available range of temperature are given in Table I. It may be remarked that the three substances last quoted in the table are all in extensive use for electric lamp filaments.

TABLE I.—VARIOUS TEMPERATURES.

	Deg. C.
Absolute zero	−273
Helium boils (0·2 mm.)	−272
„ „ (760 mm.)	−269
Hydrogen boils	−253
Oxygen boils	−183
Carbonic acid boils	− 78
Mercury freezes	− 39
Water freezes	0
Water boils	100
Tin melts	232
Lead melts	327
Mercury boils	357
Zinc melts	419
Sulphur boils	445
Aluminium melts	657
Common salt melts	801
Zinc boils	918
Silver melts	961
Gold melts	1062
Copper melts	1083
Cast-iron melts	about 1100
Pure iron melts	1500
Fire bricks soften	1400–1800
Silica softens	1500–1600
Platinum melts	1750
Silver boils	1950
Tin boils	2270
Copper boils	2310
Lime and magnesia melt	about 2400
Iron boils	2450
Tantalum melts	2900
Tungsten melts	3000
Carbon melts	?

Table II. gives examples of various flame temperatures, which we have at our disposal.

TABLE II.

Temperatures attainable in : —	Deg. C.
Bunsen burner flame	1100–1350
Méker burner flame	1450–1500
Petrol blow-lamp flame	1500–1600
Oxy-hydrogen flame	about 2000
Oxy-acetylene flame	„ 2400
Thermit	„ 2500
Electric arc	„ 3500
Electric arc (under pressure)	„ 3600
Sun	„ 5500

Some of the methods for measuring temperature with their limitations are briefly recapitulated in Table 3. I have only time to refer to one or two points. We have recently had the opportunity at the National Physical Laboratory of subjecting a number of mercury in silica thermometers to a critical examination. These thermometers which are made in England, possess in a high degree the qualities of constancy, large range, and such complete freedom for temporary zero change that I feel safe in prophesying they will inevitably replace the present International standards, which are made of verre dur.

TABLE 3 —SOME INDICATION OF THE PRESENT RANGE OF TEMPERATURE MEASURING INSTRUMENTS.

Method	Range in Degrees C.	
	Practical	Extreme
Expansion thermometers—		
Gas thermometer	Up to 1200°	−272° to 1550°
Mercury in glass	− 39° ,, 500°	− 44° ,, 575°
Mercury in silica	− 39 ,, 600°	− 44° ,, 700°
Electrical thermometers—		
Platinum resistance . .	−100° ,, 1100	−250° ,, 1400°
Thermocouples :		
— platinum alloys . .	300° ,, 1400	Up ,, 1750°
— base metals	−100° ,, 1100°	−250° ,, 1200°
Total radiation pyrometers . . .	500° ,, 1400°	No upper limit
Optical pyrometers	600° ,, 3500°	No upper limit

In regard to high temperatures most of us rely to some extent on colour in estimating temperature. Table 4 gives a very fair notion of the temperature we may reasonably associate with the colour of a

TABLE 4.—TEMPERATURE AND COLOUR OF A FIRE.

Colour	Cent.	Fahr.
" Grey," lowest discernible temp. . .	About 450°	About 850°
Very dull red	,, 500°	,, 950°
Dull red	,, 700°	,, 1300°
Cherry red	,, 900°	,, 1650
Orange	,, 1100°	,, 2000°
White	,, 1300°	,, 2400°
Dazzling white	Above 1500°	Above 2750°

fire or muffle furnace (experiment shown). The intensity of the light varies according to well-known laws which have been studied

up to sun's temperature. If we know the law of variation we can measure the temperature by the use of some kind of photometer—which is what all optical pyrometers are.

For obtaining really high temperatures electric furnaces are our only resort. Small gas furnaces can reach 1600° with difficulty; large industrial furnaces attain 1800° C. in some instances.

Mr. Cook, of Manchester, has kindly lent me for this occasion a number of electric furnaces. These are constructed by winding tubes of fire clay or alumina with nichrome or platinum wire: the external lagging is of kieselguhr. Steady temperatures up to about 1000° and 1200° C. respectively can readily be got with power from a commercial circuit of 100 or 200 volts. With thicker wires and current at lower voltage these upper limits can be appreciably extended.

For higher temperatures we have to make use of carbon or graphite, and electric heating was first applied by such means in the form of the arc furnace. Such a furnace has many inconveniences—the heating is intensely local, and there may, for example, be a gradient of 2000° C. in a single inch. There is practically no temperature control, and there is every possibility of the final product becoming largely contaminated with carbon. Most of the early isolated so-called elements have since proved to be largely carbides.

Resistance heating is usually much more convenient, and this is the principle of carbon-tube furnaces, some essential features of which were employed by Prof. Dewar many years ago. They will stand rough use, and are much more controllable than the arc furnace. It is as easy to control a temperature of 2500° C. as one of a red heat.

Such furnaces usually have their end-terminals water-cooled, and are surrounded by lagging of lamp-black or charcoal.

The furnace tubes are either straight if made of carbon (Fig. 2), or spiral if made of Acheson graphite (Fig. 3). In the latter case they are provided with an internal liner-tube of carbon. There is no special difficulty in cutting the spirals from the solid; graphite, unlike amorphous carbon, is an extremely tractable substance to machine.

We have used these carbon resistance furnaces a great deal at the National Physical Laboratory, and Mr. Greenwood, at Manchester, carried out his experiments on boiling metals by the aid of such a furnace. The boiling of a metal (shown) forms a not-impossible lecture experiment, and a projected image of the surface of boiling tin displays all the usual phenomena of ebullition. The heating up of carbon is somewhat strikingly shown by passing a heavy current through a thin broad carbon strip provided with water-cooled terminals (experiment shown). The stream lines of heat flowing from one terminal to the other are well illustrated at one stage of the heating.

Among other methods of electric heating are the induction furnace, which is of great value in refining crude materials, and the flame spark, in which it is possible to volatilize as refractory a substance as an incandescent gas mantle.

Some time ago we endeavoured at the National Physical Laboratory to make a furnace for very high temperatures without employing carbon. The introduction of the Nernst lamp was suggestive. It was found that a great number of substances could be made to act like a Nernst filament, e.g. a piece of the stem of a churchwarden pipe, if sufficiently strongly heated, can be made to conduct electricity well enough to become incandescent. Carborundum crystal behaves similarly, and requires no initial heating (experiment shown) ; in this
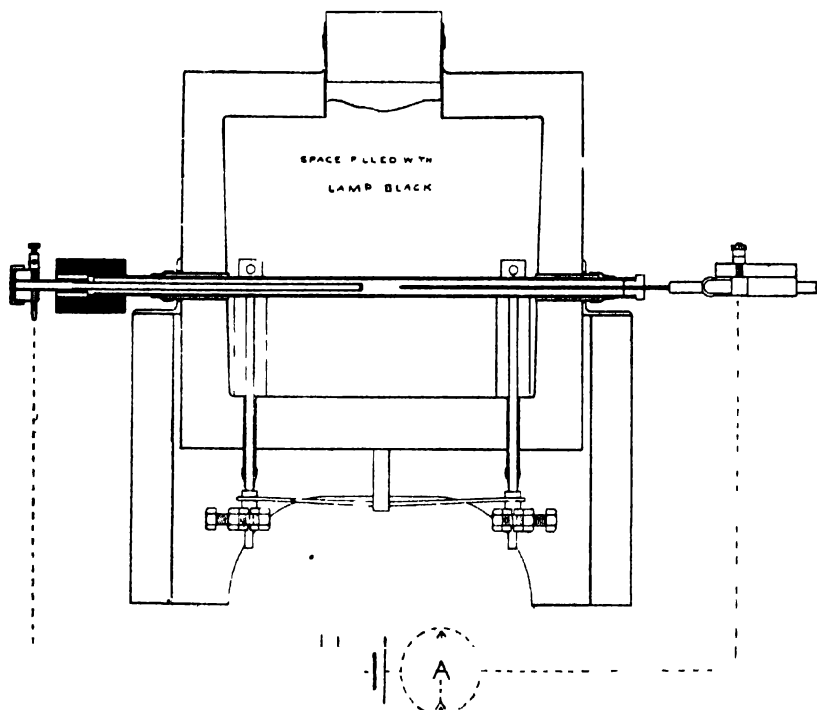

FIG. 2.—SMALL MODEL STRAIGHT CARBON-TUBE FURNACE.

case the temperature can be raised high enough to volatilize off the silicon, which burns, forming a cloud of silica. A cascade furnace was constructed on these lines : a tube made up of zirconia and a little yttria was raised by means of an insulated nickel winding to 500° or 600°, at which temperature the tube conducts sufficiently well to enable a heating current to be passed through it. There is no difficulty in melting platinum, for example, in such a furnace using a quite small heating current (about 2 amps.) A zirconia tube from such a furnace was taken out after it had been run for six

months or so ; it was then found to be quite translucent. The possibility of constructing in such a way refractory gas-tight materials at once suggested itself, and we proceeded to manufacture "pottery" at high temperatures. Great difficulties have been encountered in the experiments. Whereas, for example, the potter in baking his wares at temperatures up to 1300° C. looks for a shrinkage of 5 per cent. or so, we were confronted with a shrinkage of 37 per cent. For the purposes of the fritting we employed carbon-tube furnaces of one of the types mentioned above. Now it sometimes happened that the outer surface of the zirconia tubes, instead
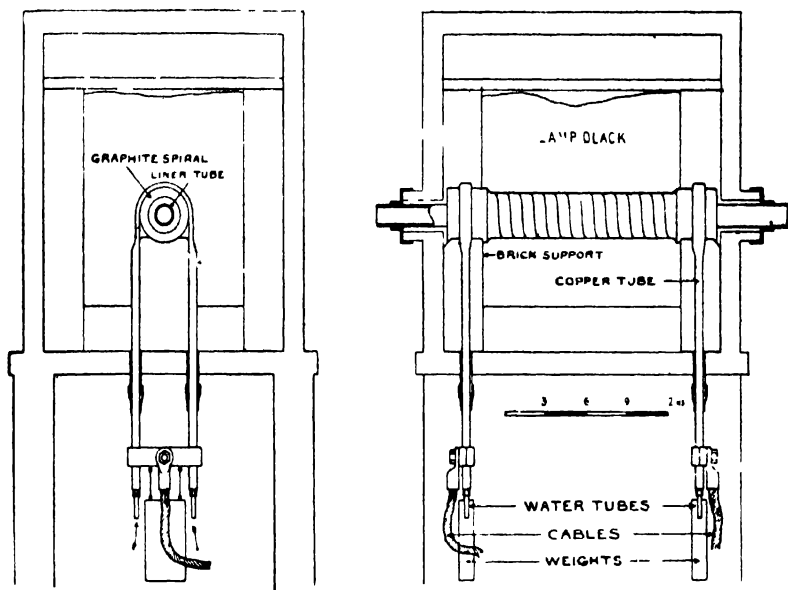

FIG. 3.—CARBON-TUBE FURNACE WITH GRAPHITE SPIRAL HEATER.

of having the white and hard appearance of the rest, was found to be carburised and crumbly after baking. The action was not merely superficial, but extended to an appreciable depth. On the other hand the inner surface of the tube, though freely open to the furnace atmosphere, was much less affected. The blackening occurred to a much less extent if the tube was shielded. It seemed as though particles, possibly electrified, were shot off from the carbon walls of the furnace across a space of some 5 or more mms. into the material of the refractory tubes. Dr. G. W. C. Kaye and I were led to investigate the cause of these phenomena, and yesterday we gave an account of some of the results to the Royal Society. I propose to

devote the remainder of my lecture to a description of the methods employed and the results obtained in what proved to be a very interesting investigation.

Many experiments have been conducted, notably by Prof. O. W. Richardson, on the corpuscular emission of electricity from carbon at

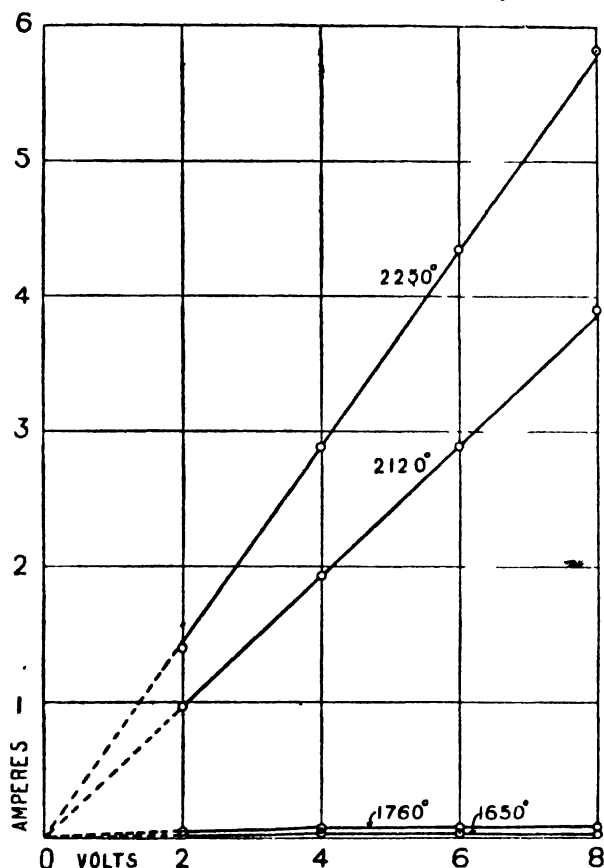
FIG. 4.—RELATION BETWEEN IONIZATION CURRENT AND APPLIED POTENTIALS FOR A 1 CM. GAP BETWEEN THE ELECTRODES.

very low pressures, but scarcely anything is recorded for pressures approaching atmospheric. Positive ions and material particles are also discharged by carbon, as well as by hot metals, at suitable temperatures and pressures.

It is to be understood that in all the experiments now to be

described the pressure remained atmospheric, and alternating current was employed for heating. Access of air to the interior of the furnace was prevented by windows at each end, perforated as required.

In the early experiments we inserted within the carbon furnace tube two insulated carbon electrodes, one of them being hollow, so that a Siemens optical pyrometer could be sighted through it. The two electrodes were joined externally to an ammeter and a battery of cells (see Fig. 2), and we proceeded to determine current-voltage
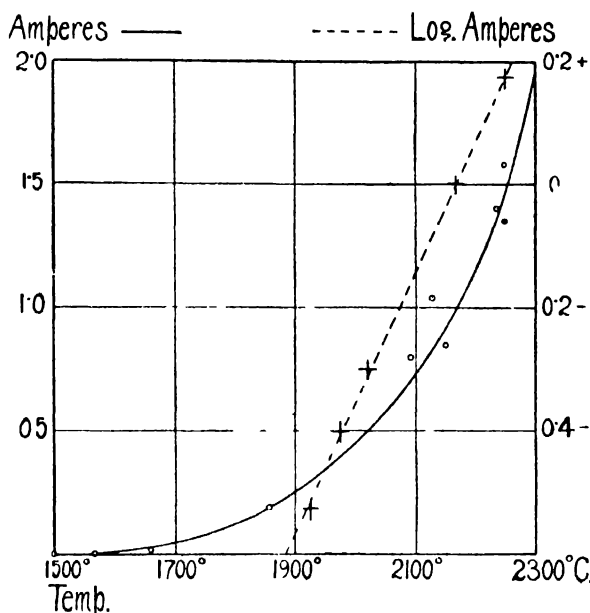

FIG. 5.—THE FULL LINE CURVE SHOWS A RELATION BETWEEN IONIZATION CURRENT AND TEMPERATURE, FOR AN APPLIED POTENTIAL OF 2 VOLTS ON A 1 CM. GAP BETWEEN THE ELECTRODES The dotted straight line is plotted from the log. of the current and the temperature.

curves at various furnace temperatures. Some of these curves are shown in Fig. 4 for an electrode gap of 1 cm. No appreciable current could be detected below 1400° C. with applied potentials up to 8 volts, but as the temperature rose the current rapidly increased until at 2500° or more currents up to 10 amperes were recorded. At the lower temperatures the currents soon attain what appear to be saturation values. At higher temperatures there is a linear relation between potential and current. As the length of the gap increased the current diminished at a regular rate ; but the decrease was small.

Fig. 5 exemplifies the exponential relation between temperature and current for a 1 cm. gap and an applied potential of 2 volts. The dotted straight line was plotted to axes of temperature and logarithm of current.

The magnitude of the currents made it evident that in spite of the high pressure the atmosphere of the furnace was ionized to an unusual degree at high temperatures, and we were led to investigate the effect of temperature alone. The battery was accordingly cut out
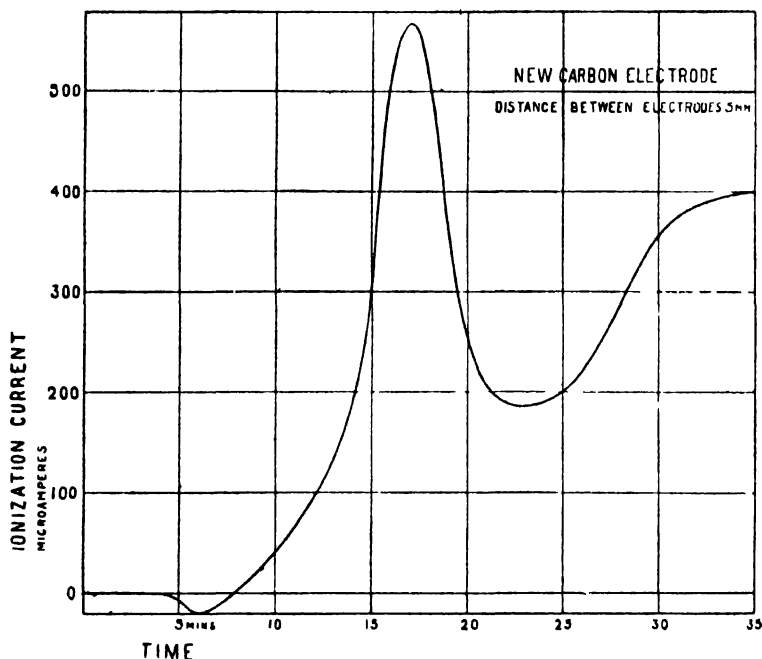
FIG. 6.—RELATION BETWEEN IONIZATION CURRENT AND TIME WITH A STEADILY RISING TEMPERATURE. The "cold" electrode was water-cooled; the hot electrode was of new carbon. No potential was applied.

and one of the two carbon electrodes was mounted on a sliding carriage so that it could, at will, be moved in or out of the hot part of the furnace, i.e. away from the fixed electrode or back towards it. The movable electrode would thus be temporarily cooler than the fixed electrode which remained steadily in the furnace. The ammeter in the circuit indicated a current which amounted to 2 milliamperes at 1400° and nearly 2 amperes at 2500°; the cooler electrode was the positive one. The currents died away when the two electrodes attained the same temperature.

The production of an alternating current of very low frequency is thus rendered possible by the use of some periodic device. In one form of the experiment (shown) the movable electrode is attached to a crank which, rotated slowly by clockwork, performs the necessary displacement of the electrode within the furnace. The ionization currents produced are sufficient to make a nest of small glow-lamps light up brilliantly, the illumination waxing and waning as the movable electrode moves in and out.
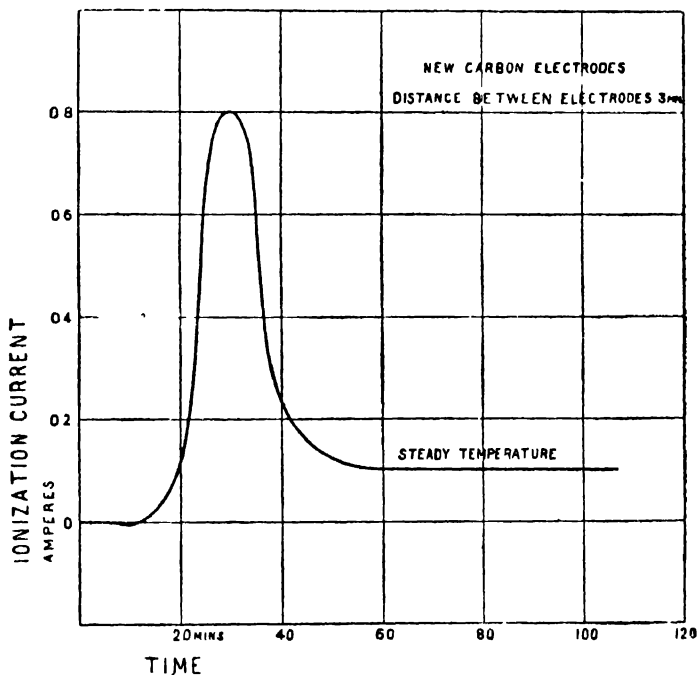
FIG. 7.—RELATION BETWEEN IONIZATION CURRENT AND TIME FOR TWO NEW CARBON ELECTRODES, ONE HOT, THE OTHER WATER-COOLED. No potential was applied. The temperature was rising for the first fifty minutes, and was afterwards steady.

We have been able to repeat some of these results with furnaces of a non-electric character.

In a further series of experiments, various modifications were introduced. The two electrodes were replaced by two co-axial tubes which were mounted within the furnace. The central smaller tube was of brass, through which a rapid current of water was sent ; this formed the " cold " electrode. The surrounding larger tube of carbon constituted the hot electrode, and received its heat from the furnace.

The electrodes were insulated as before, and into the annular space between them hydrogen or nitrogen was continually passed. No potential was applied, and the currents we obtained with a steadily rising temperature and a new carbon electrode are shown in Fig. 6. It will be seen that there was first a small " positive " current (which would be produced by positive ions crossing from the hot to the cold electrode), which soon changed into a much larger " negative " current (in the usual direction) ; the intensity of the latter dropped, and then showed a progressive increase with temperature. On taking down the apparatus we found that the brass tube was coated over most of its length with a thick and coherent deposit of carbon which had evidently crossed over from the hot electrode. Towards one end the deposit was rarer and whitish—presumably silica. We associate the maximum negative current of Fig. 6 with the passage of silicon and other impurities, which are volatilized at about 2000° C. out of the carbon electrode. On a second heating neither positive rays nor a negative maximum were detected, but the ionization current increased steadily with temperature. The transference of carbon from the hot electrode to the cold may prove to be a complete explanation, not only of the contamination phenomena which gave rise to these experiments, but also of the comparatively large accompanying currents.

Fig. 7 illustrates the results obtained when steps had been taken to increase the difference of temperature between the hot and cold electrodes. The carbon was new, and the negative maximum again appears. Afterwards the furnace temperature was steadied, and the ionization current also kept steady in consequence. It will be noticed that we were now dealing with currents amounting to large fractions of an ampere, and the experiments may fairly be regarded as providing a novel means of generating electricity. Their direct bearing on the problems of the electric arc and the carbon filament lamp is obvious, and we are continuing the research with a view to elucidating the many underlying phenomena.

[J. A. H.]

Friday, March 15, 1912.

His Grace the Duke of Northumberland, K.G. P.C. D.C.L. LL.D. F.R.S., President, in the Chair.

Frederick Soddy, Esq., M.A. F.R.S.

The Origin of Radium.

The philosophical explanation of radioactivity arose out of some very simple chemical observations on the nature of the radioactive process. The apparently permanent and constant radioactivity of radioactive substances in general consists of two parts. One part cannot, as a rule, be separated from the substance, whilst another part is readily separated by many ordinary chemical and physical operations. The latter part is often the larger part of the whole radioactivity, but it is associated frequently with a practically infinitesimal proportion of the material. Naturally, the first explanation to present itself was the ordinary one that the radioactive substance is not homogeneous, but consists of a mixture of more than one radio-element. In this way Mme. Curie accounted for her analysis of the radioactivity of pitch-blende, and the separation from the preponderating radioactive constituent, uranium, of new radio-elements in minute amount, to which the names radium, polonium, and actinium were given. Similarly, Sir William Crookes, who separated by chemical methods the β-activity of uranium compounds, gave the name uranium X to the constituent responsible for this activity.

In a chemical examination of the radioactivity of thorium compounds ten years ago, Professor Rutherford and I found that one portion of the activity was separable from the thorium by chemical methods, and to the constituent responsible for this separable activity the name thorium X was given. Then an astonishing observation was made. Unlike any other chemical separation which had hitherto been carried out, it was found that thorium, after having been deprived of thorium X by simple chemical processes, spontaneously regenerated this constituent with lapse of time. After a month's interval from the separation a new quantity of thorium X could be obtained from the thorium, the activity of which was as great as that obtained in the first separation. In the same interval the activity of the thorium X first separated completely decayed, according to an exponential law. This continuous regeneration of the constituents responsible for the

separable portion of the radioactivity was found to occur not only with thorium, but also with radium and with uranium. If a chemist observed that after a substance had been separated from impurities these impurities made their appearance again with the lapse of time, he would scarcely credit his observations. If such observations were confirmed and shown to be the invariable consequence, impurities after chemical separation being regenerated with lapse of time, the view that the elements were the ultimate unchanging constituents of matter would be undermined. The theory of atomic disintegration was founded on facts of this simple chemical nature, and not, as has sometimes been asserted, on any mathematical or physical theories as to the nature of the atoms of matter. The question immediately arose whether over long periods of time the intensely radioactive constituents separated from uranium minerals were being regenerated by the disintegration of one or more of the other elements in these minerals ; and this question, as regards radium, forms the subject of the lecture.

The law of radioactive change is the simplest possible expression of what has been termed by chemists Mass Action, and has been familiar to them as " the law of mono-molecular reaction " since the classical researches of Wilhelmy in 1850, and of Harcourt and Esson in 1865. The "velocity" of the change, that is the quantity changing in the unit of time, is always some definite fraction, signified by the symbol λ, and known as the radioactive constant, of the amount remaining unchanged. The period of average life of the changing atom is the reciprocal of this radioactive constant, that is $1/\lambda$. The peculiarities of radioactive changes depend upon the fact that frequently several successive changes occur in series, a substance A changing at a definite speed according to the law stated and forming a product B, which changes according to the same law but at its own peculiar rate, forming the product C, and so on. All through, the number of atoms, of any one member of the series, changing in a given time is the number of atoms of the next product formed, the general differential equation being

$$\frac{d\,Q}{d\,t} = \lambda_P\,P - \lambda_Q\,Q$$

where P and Q are the quantities of *any* two successive members in the series and λ_P and λ_Q, their radioactive constants.

The machine exhibited (Fig. 1), of which a full description will be published separately, is designed to illustrate radioactive change, even in some of its more complicated cases, and to draw the graphs connecting the quantity of the radioactive substance with the lapse of time, when the substance in question is the first, second, third, or, in certain cases, the fourth product of the successive changes. It consists of three separate units, one of which is sketched in Fig. 2. The height of the nut on its screw represents the quantity of the radio-
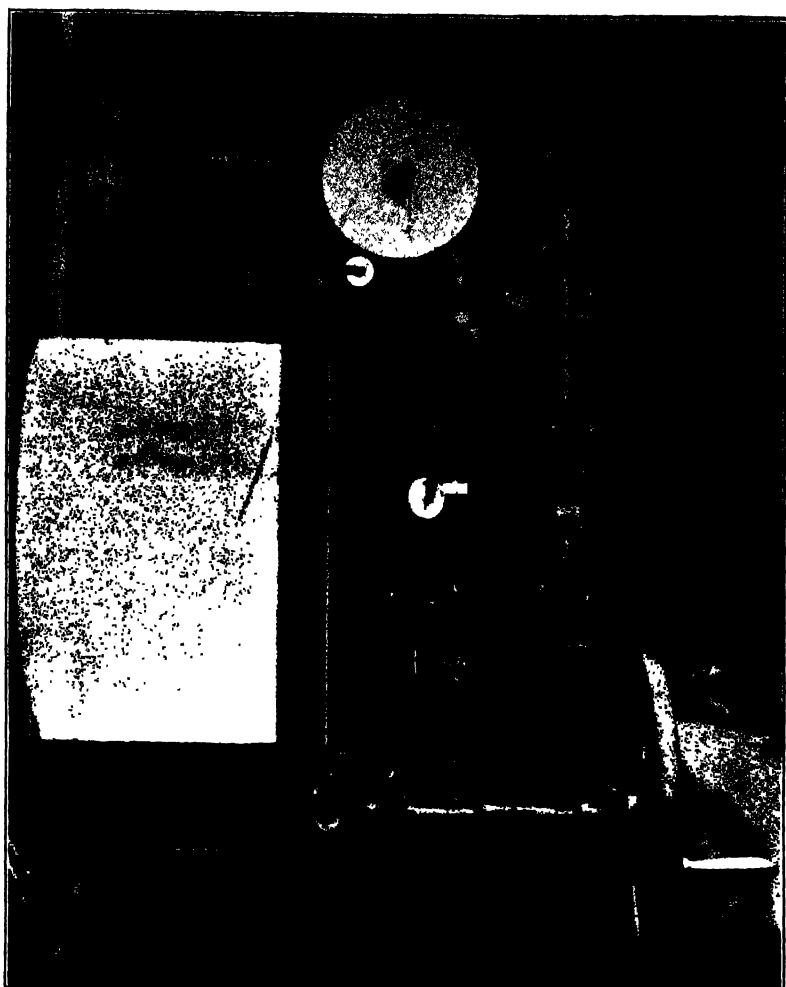
FIG. 1.

active substance in question. This height is magnified and communicated by pulleys and cords to a crayon-holder moving vertically over

A. LOCK-NUT.

B. RUBBER-TYRED DISC.

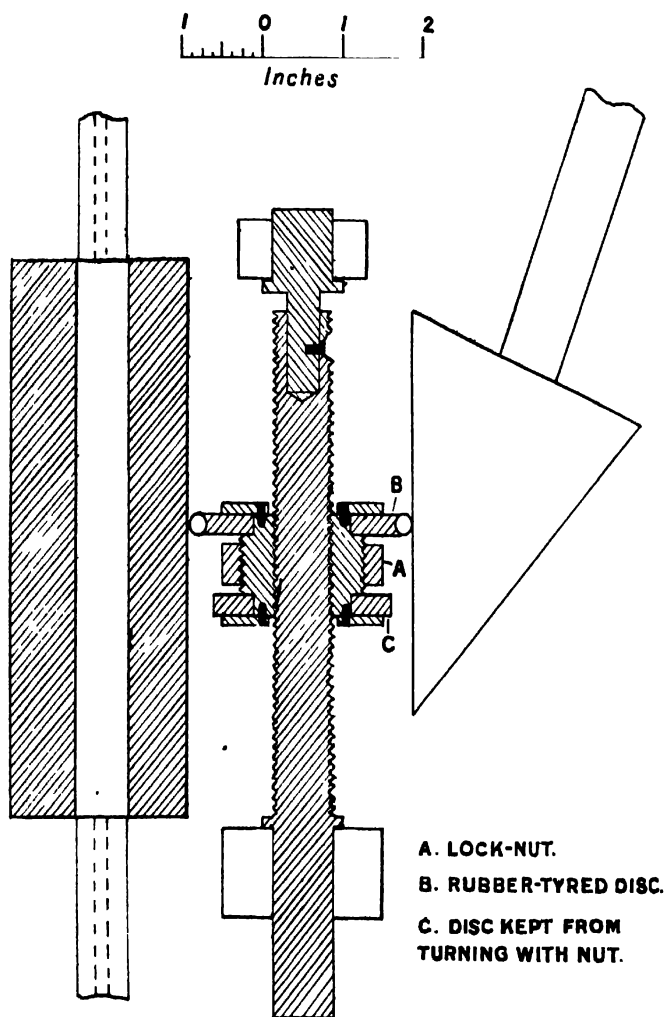C. DISC KEPT FROM TURNING WITH NUT.

Fig. 2.

a paper roller geared to the main shaft, the paper moving horizontally in a vertical plane. The rubber-tyred nut is constantly being turned down on the screw by a rough cone, driven at constant speed from

the main shaft, which presses against it. The rate at which it moves downward is always proportional to the height of the nut above the point of the cone, that is to the quantity of substance remaining unchanged. If the screw does not turn, the nut descends exponentially with the time, illustrating the exponential decay of activity of a single radioactive substance when left to itself. On the other hand if the *screw* is now turned at constant speed in the direction to screw the nut up, the nut mounts according to the usual law of the regeneration of a radioactive constituent after it has been separated, to the height such that it is turned down by the cone as fast as it is turned up by the screw. At this point it is in equilibrium, precisely analogous to radioactive equilibrium, and does not move however long the machine is driven. The rubber-tyred *nut* communicates its turns by means of a roller and gear-wheels to the *screw* of the next unit above, in accordance with the requirement that the quantity of one member changing is the same as that of the next member produced. Thus the fall of the nut by virtue of the cone turning it and screwing it down represents $- \lambda_Q Q$; the rise of the nut, by virtue of the screw turning and screwing the nut up, represents $+ \lambda_P P$ of the general differential equation. The various radioactive constants are imitated (1) coarsely, by using screws with threads of different pitch ; (2) finely, by varying the speed of the driving cone with reference to that of the main shaft by a suitable arrangement.

To imitate the frequent case where the period of the radioactive substance is infinitely long compared to the time of the experiment, the rubber-tyred disc may be arranged, by undoing a lock-nut, to " free wheel " without turning the nut. This then corresponds to a screw of infinitely fine pitch, or to a radioactive substance of infinitely long period. The numerous cases of radioactive change discussed in the lecture were imitated by graphs drawn by the machine.

In addition to offering a consistent explanation of all the known facts that had been accumulated in radioactivity, the theory of atomic disintegration suggested a large number of new problems. Only two of these original problems remain not yet completely answered. One had to do with the nature of the ultimate product or products of the disintegration of the atoms of the two primary elements, uranium and thorium. This problem may be likened to the task of trying to find a meteor after its flight, when its energy is spent and nothing but the matter remains. Much indirect evidence points to lead as the final product of uranium, although no direct proof has been obtained, whereas for the case of thorium there is still no hint of the answer. The other had reference to the origin of radium. This element in the intensity of its activity, and, therefore, in the rapidity of its disintegration, resembles the short-lived active constituents uranium X and thorium X, whilst in the apparent permanence of its activity it resembles the primary radio-elements. Even the first rough estimates indicated that the period of

average life of radium was not greater than a few thousand years. The present estimate, due to Rutherford, is 2500 years. A few thousand years hence the radium in existence to-day will for the most part have disintegrated. Very little of the radium in existence at the time the Pyramids were being built can still exist. Hence arose one of the most interesting and crucial of the problems of atomic disintegration. Does the regeneration of radioactive constituents, observed in the cases where the period is short compared to the span of human life, apply also to radium—to an element, that is, with a definite spectrum, atomic weight and chemical character, filling a vacant place in the periodic system, and forming one of a family of common elements ? After the separation of radium from a mineral does the non-radium part of the mineral grow a fresh crop with lapse of time, the quantity present before separation being the balance or equilibrium quantity when the rate of production is equal to the rate of supply ? A somewhat similar prediction made with reference to the production of another well-defined element, helium, in the radio-active process had only to be tested, as it was first in 1903 by Sir William Ramsay and myself, to be proved correct. The question, however, of the origin of radium is still, in spite of many discoveries, not entirely solved.

At first sight the experimental trial of the view appeared easy. This problem is not analogous to the finding of a meteor after its flight is spent. The quantities of radium which can be detected and recognized unequivocally by radioactive methods are thousands of times smaller than can be detected even by the spectroscope, sensitive as the spectroscopic test of radium is. The first product of the dis-integration of radium is a gas, the radium emanation, and the test for radium consists in sealing up a solution of the substance for a month, then boiling the solution in a current of air, and introducing this air into the electroscope. For the instrument employed and shown (Fig. 7), a millionth of a milligram of radium would be rather an undesirably large quantity, whilst a few hundredths of this amount is the best suited for accurate measurement. The volume of radium emanation, measured at N.T.P., obtainable from one gram of radium is only 0·6 cubic millimetre. If a thousandth part of this quantity were distributed uniformly through the air of this room, estimated as 50,000 cubic feet, or about 1⅔ tons by weight, and the electroscope were then filled with the air of the room, it would produce an effect much greater than any dealt with in the work to be described. (The effect of breaking a tube containing the emanation in equilibrium with 3 mg. of radium outside in front of the fan supplying air to the building was demonstrated by the electroscope.)

Only two primary radio-elements, uranium and thorium, were known changing sufficiently slowly to account for the maintenance of radium in the earth to-day. Indeed, these two elements are the only ones known with atomic weights greater than that of radium, and are

the only ones to choose between, if radium is produced by the known process in the disintegration of one element, rather than by the at present entirely unknown process consisting of a synthesis of several together. Of these two, since Mme. Curie discovered radium in minerals containing large quantities of uranium, it was natural to select uranium as the probable primary parent in the disintegration of which radium is produced. If uranium were the direct parent of radium, 100 grams of uranium, purified chemically from radium, would generate a fresh quantity of radium easily detected by the instrument shown after the lapse of only a few hours.

In preliminary experiments started nine years ago, a kilo of uranyl nitrate (= 500 gr. of uranium) was carefully purified from radium by precipitating sulphate of barium in its solution. The solution was preserved in a closed vessel, and tested from time to time. After 500 days it was found that the quantity of radium had increased by an amount, which although excessively minute, was about one hundred times as much as the radium initially present. The methods of testing for radium were not then so accurate or refined as those later introduced by Strutt and Boltwood, but there is no reason to doubt their general trustworthiness. The observed growth of radium was, at most, only one thousandth part of what, according to existing data, should have been produced if uranium were the direct parent of radium. Small as it was, however, this was the first observation of a production of radium. It indicated the existence in commercial uranium compounds of a substance capable of generating radium with the lapse of time. In the meantime the character of the problem had changed. As a simple consequence of the theory of atomic disintegration, it follows that, if uranium is the parent of radium, proportionality must exist between the quantities of radium and uranium in all radioactive minerals, which have not been altered by external agencies whilst contained in the earth's crust. The quantity of radium after the lapse of some tens of thousands of years will come into equilibrium with that of the uranium when as much radium is produced as disintegrates in each unit of time. Then $\lambda_P P = \lambda_Q Q$ of the differential equation, so that the ratio between the quantities must be the same as the ratio between the periods of average life of the two elements. Researches carried out by McCoy, Strutt, and Boltwood, particularly the last two, proved that this was the case. The ratio of radium to uranium in all unaltered minerals is, on present data, $3 \cdot 1 \times 10^{-7}$ to 1, that is, there are 310 mg. of radium per ton of uranium. From this ratio, the period of uranium calculated from that of radium is 8,000,000,000 years. Thus was obtained fairly conclusive, though indirect, evidence that uranium is the primary parent of radium. Unfortunately it still remains the only evidence available. To account for the excessively slow growth of radium in the first uranium preparations studied it was necessary to suppose that between the uranium and

radium an intermediate product existed of period of life great by com-
parison with the time of the experiment. Such a product would
enormously retard the initial growth of radium. Its existence com-
plicates what first appeared as a very simple problem in many other
ways. It is no longer a question of simply detecting a growth of
radium. It is necessary to measure the form of the growth-curve
accurately.

In the first place this intermediate parent must be present in
uranium minerals, and therefore, to greater or less extent, in com-
mercial uranium salts. The mere separation of radium therefrom
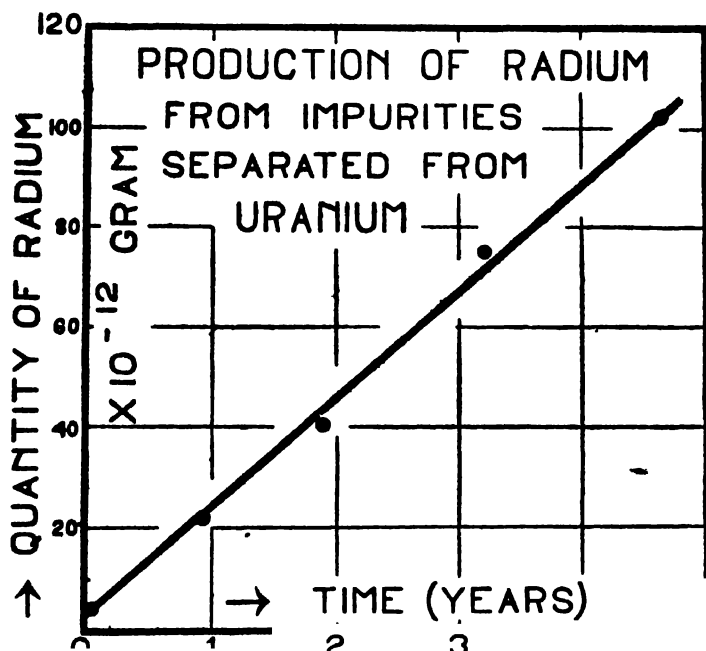
FIG. 3.

initially, as in the first experiment, is not sufficient purification. In
addition every trace of the intermediate parent must also be sepa-
rated, or a growth of radium will not prove that uranium is the
parent. On this account, in conjunction with Mr. T. D. Mackenzie,
a fresh series of experiments were begun in Glasgow in 1905, in a
new laboratory uncontaminated by radium. Three separate quanti-
ties, each initially of 1 kilogram of uranyl nitrate, were purified by
repeated extraction with ether, which was considered to be the method
most likely to separate all the impurities, not merely the radium.

Observations on these preparations have now been in progress for six or seven years. At the same time a portion of the impure fraction separated from the original material was sealed up, freed from initial radium by the barium sulphate method, and tested for radium from time to time along with the pure uranium preparations. The diagram (Fig. 3) shows the growth of radium in this impure fraction. The unit used for expressing the quantity of radium is 10^{-12} gram. It confirms unequivocally the original observation that a substance is present in commercial uranium salts capable of generating radium and not removed from it by the barium sulphate method used first for separating the radium, but separated, at least mainly, by the ether method.

The methods of storing the preparation, and of extracting the emanation from the solutions and measuring it, are illustrated in
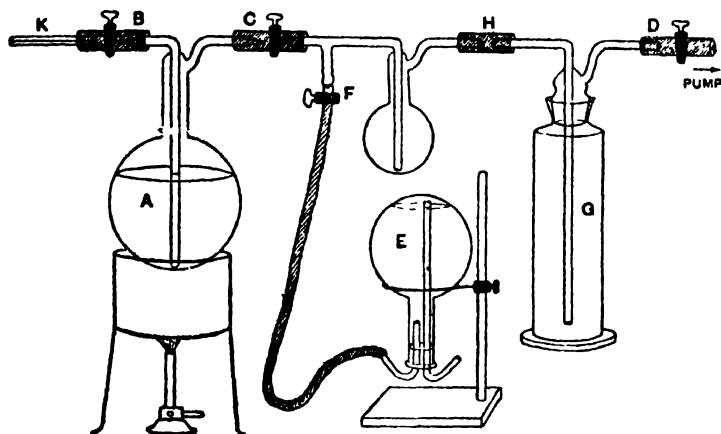
FIG. 4.

Figs. 4 to 8. Figs. 4 and 5 represent a diagram and photograph respectively of the arrangement used for boiling out the emanation from the uranium in the flask A (Fig. 4) under reduced pressure, and of collecting it in the bottle G, from which it is expelled into the exhausted electroscope (Figs. 6 and 7). The leak is taken after 3 hours, the electroscope being kept charged throughout the whole interval. The electroscope is calibrated by similar tests with solutions containing known small amounts of pitchblende of known uranium content. Fig. 8 represents a more recent experiment with a very large quantity of uranium in which a reflux condensor is sealed into the flask. This addition makes it possible to work with large volumes of fluid even more easily and accurately than for the older quantities.

FIG. 5

Fig. 7.

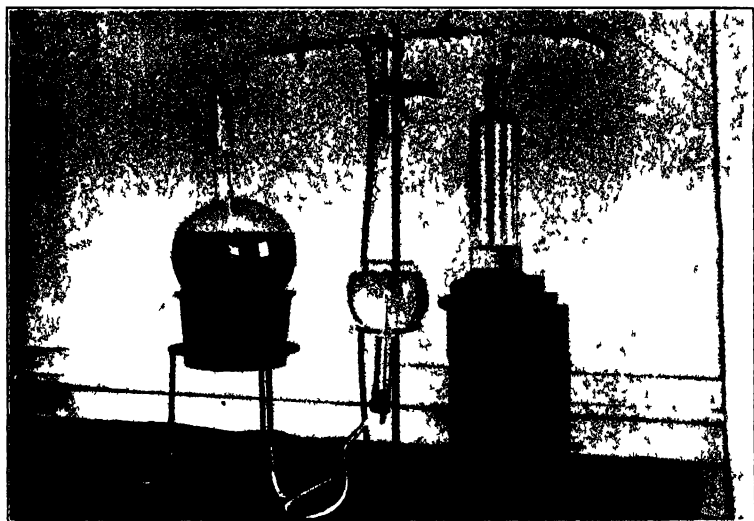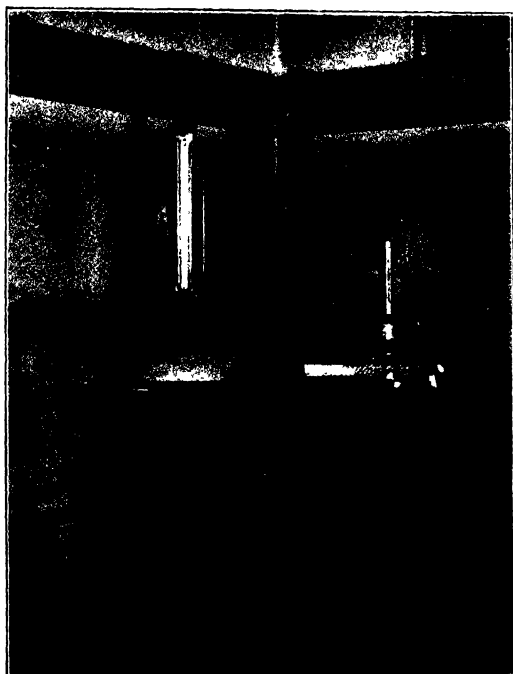In the meantime a cognate discovery of first importance was made by Boltwood, in America, who proved that actinium preparations obtained from uranium minerals, and initially free from radium, grow a fresh crop of radium with lapse of time. The growth is not by any means a very minute one as in my experiments, in which the growth can only be put beyond all doubt after the lapse of years. The growth of radium from constituents separated from minerals can be readily detected and measured in a relatively short space of time. The curve shown (Fig. 9) is taken from a paper by Keetman (Jahr. Radioact. Elektronik, 1909, vi. 270), who has worked upon this parent of radium in Germany. Although the total quantity of radium represented by this curve is only nine millionths of a milligram, it is enormous compared with that shown by the other diagram (Fig. 3), in which the quantity of radium produced in a period about eight times longer is
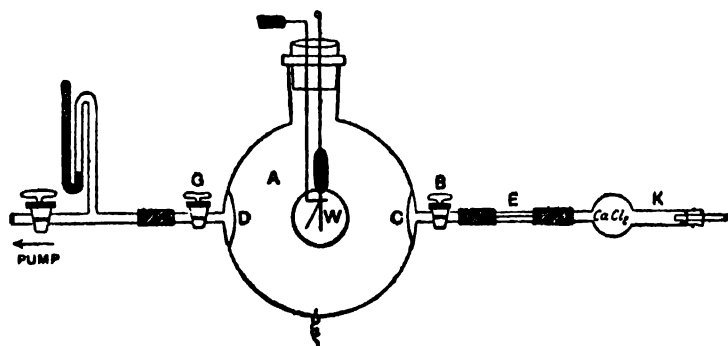
FIG. 6.

nearly a hundred times less. Further work on this parent of radium proved that it was not actinium, but a new radio-element admixed with it, which Boltwood called ionium. It is radioactive, and its radiation consists entirely of α-rays of very low range. The chemical nature of this ionium is absolutely identical, so far as is known, with that of thorium, and it cannot be separated from it. On the other hand, it is easily separated from any mixture, however complex, by adding a trace of thorium and separating and purifying the latter. It is interesting to note that no less than three at least of the known radio-elements—ionium, radiothorium, and uranium X - are absolutely identical in chemical properties with thorium. This complete similarity with known elements is one of the features of the chemistry of the radio-elements.

Returning to the experiments with the uranium solutions purified by ether, Fig. 10 shows the growth of radium therein. The three

curves labelled I, II, III, refer to these preparations. No. III was the last prepared, after experience with the others, and contained both the greatest quantity of uranium and the least radium initially. No. IV refers to a much later experiment with no less than 6 kilograms of uranyl nitrate, purified by repeated crystallization in the course of other work. In all, there has been a distinct growth of radium, but it is so small, and the period over which the measurements extend is so prolonged, that the errors of the individual measurements are relatively great. The general scope of the curves, as indicated in the figure, are, however, probably not far wrong. A conservative view to take is that in all cases the curves are straight lines. There
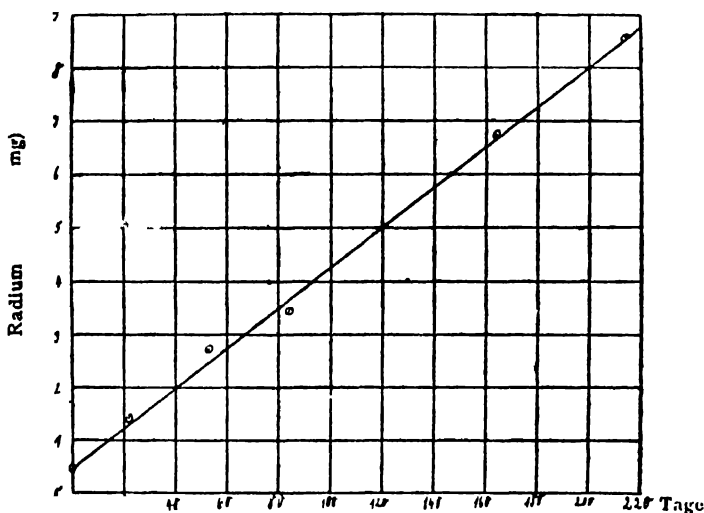
FIG. 9.ᵃ

is some indication in No. I of an increasing slope, but it is negatived by the evidence of Nos. II and III.

The quantity of uranium in the four preparations differs widely. In Fig. 11 the curves are replotted in a different way to eliminate this difference. The ordinates represent the quantities of radium formed in terms of the amounts of radium in equilibrium with the uranium. The equilibrium amount is the amount that theoretically should be formed after the lapse of sufficient time, if uranium is the ultimate parent of radium. It will be seen that the slopes of the four curves are all different and diminish in order, the growth in the first being the greatest, and in the last, after all the experience in methods of purification, the least. This is additional evidence that,
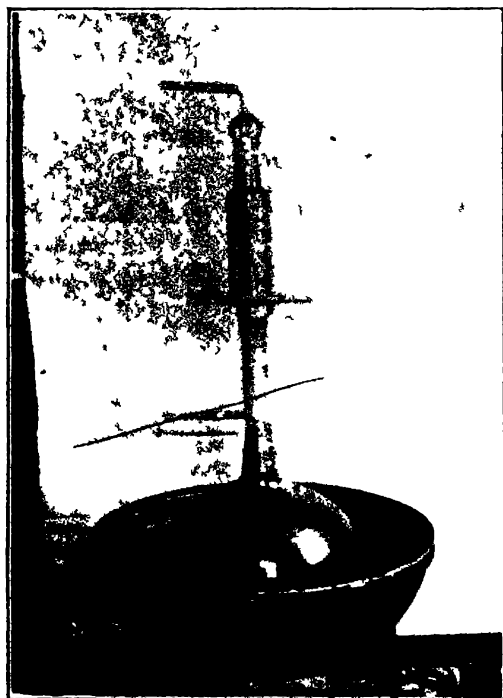
FIG. 8.

so far, the radium formed is derived, not from the uranium, but from varying infinitesimal quantities of ionium still unremoved by the purification processes.

Taking No. III as the best of the first batch of preparations, the growth of radium therein is only about $\frac{1}{30000}$ part of what would have occurred if uranium were the direct parent of radium. Some idea of the minuteness of the quantities of radium indicated by these curves can be got by the following consideration. Radium bromide at its present price costs about 16*l.* per milligram. For the element, radium, this is at the rate of 750,000*l.* per ounce. The diagram (Fig. 10) is 2 feet high. To represent a pennyworth of radium on
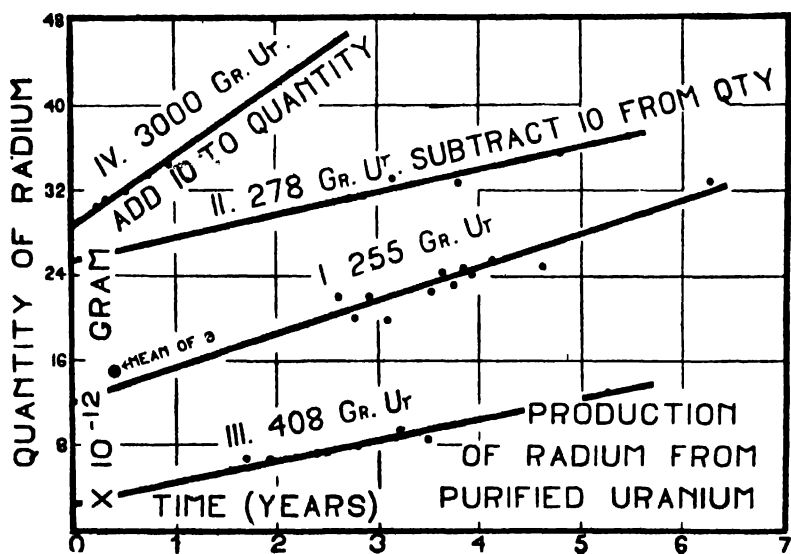
Fig. 10.

this scale would require a diagram over 6000 feet high, whereas to represent Keetman's curve (Fig. 9) would require one as high as St. Paul's Cathedral.

These results, therefore, confirm absolutely the view that uranium does not produce radium directly. As Rutherford first showed, if ionium is the only long-lived radio-element between uranium and radium, the growth of radium from uranium must initially be proportional to the square of the time, and should be represented by the equation $R = 6 \times 10^{-8} \lambda T^2$, where R is the radium formed per kilogram of uranium, T is the time in years and $1/\lambda$ is the period of

ionium. (As was shown with the machine, with all the nuts free-wheeling to imitate radio-elements with periods infinitely long compared with the time of the experiment, when no intermediate substance intervenes, the growth is a straight line as in Figs. 3 and 9, when one intervenes the curves rise at a rate proportional to the square, when two intervene, according to the cube of the time.) Hence, if uranium is the primary parent of radium, it is to be expected that the rate of growth of radium from the preparations will increase as time goes on according to some power of the time higher than unity. As Fig. 10 shows there is still no evidence of this increase of slope in any of the
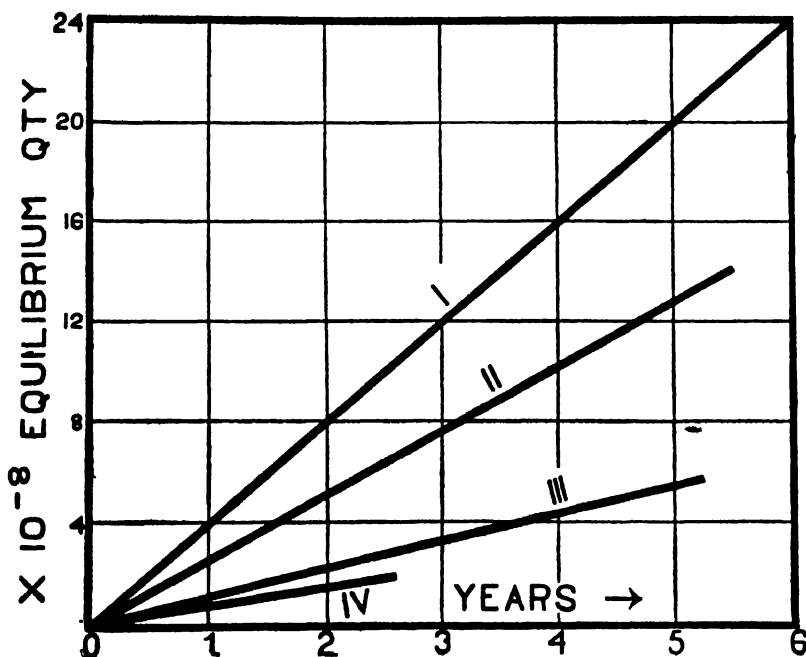
FIG. 11.

preparations. This indicates, either that the period of ionium must be enormously long, or that several intermediate long-lived members intervene. If ionium is the only intervening member a *minimum* possible limit to its period may be arrived at by applying the above equation to the results. If it is assumed that the growth observed is due to uranium and that no ionium was initially present, the minimum periods calculated in the several experiments are as follow: No. I, 28,000 years; No. II, 41,400 years; No. III, 80,000 years; and No. IV, 69,200 years. Since, in all, certainly some of the

growth is due to ionium initially present, the period of ionium must certainly be greater than the longest of these periods. We may safely conclude, if ionium is the only intermediate member, that its period is *at least* 100,000 *years*. This is 40 times longer than the period of radium itself.

Entirely independent confirmation of this conclusion was obtained in another way. The gap in our knowledge is, strictly speaking, not between uranium and ionium, for the direct product of uranium is well known and is called uranium X. It gives β-rays alone in disintegrating and has a period of only 35·5 days, so that in all the preceding work it has not been necessary to take it into account. It would retard the growth of radium inappreciably. But, if the view is right, the product of uranium X must be ionium, which gives α-rays. Concomitantly with the rapid decay of the intense β-rays of uranium X there should occur a growth of α-rays due to the ionium produced. Whether these α-rays can be actually detected will depend on the period of ionium. Fifty kilograms of pure uranyl nitrate were presented to me by Dr. Beilby, and the uranium X out of this quantity was separated, in the first place by fractional crystallization of the material. The experiment consisted in watching for the growth of a very feeble α-radiation during or subsequent to the decay of the β rays. Owing to the fact that the β-rays are readily deviated by a magnet, the intense β-radiation of the uranium X was largely suppressed, and any α-radiation remaining could be measured from day to day, as the β-rays decayed. This experiment has been repeated many times, but with completely negative results. There always was a feeble α-radiation, due to impurities, but it remained constant throughout. Neither during, nor yet, several years after the separation of the uranium X, has there been any detectable growth of α-rays. Actinium was also looked for, as the origin of this element, like that of radium, remains unexplained, but the result also was completely negative. The product of uranium X remains unknown, and if it be ionium, the period of the latter substance must be enormous. The minimum period it could possess, calculated from these negative results, is 30,000 years. This, then, confirms the conclusion of the first totally distinct set of experiments, that ionium must have a period very much greater than that even of radium.

Marckwald and Keetman have since concluded that uranium X is identical in chemical behaviour with thorium, and therefore with ionium. This conclusion has been confirmed by Mr. Fleck in my laboratory after an exhaustive series of tests, not yet published. Hence in the repeated separation of uranium X from the large quantity of uranium the very best method was adopted unwittingly for removing ionium at the same time. This accounts for the gratifying result with preparation No. IV, which was the purest fraction of the large quantity obtained after numerous crystallizations of the original material.

The question arose whether by any means an upper limit, or maximum value, for the period of ionium could be assigned. By the law already discussed there must be many times as much ionium as radium in uranium minerals, and if the actual ratio were known the period of ionium could at once be found. For example, if the period were 100,000 years, there should be $12 \cdot 5$ grm. of pure ionium per ton of uranium. Auer von Welsbach, in a masterly chemical separation of the rare-earth fraction from 30 tons of Joachimsthal pitchblende, separated a preparation, which he described as thorium oxide, containing ionium, the activity of which was measured by Meyer and von Schweidler. To obtain a maximum estimate for the period of ionium, I assumed that Welsbach's preparation was in reality pure ionium oxide (which it certainly was not, as it gave the thorium emanation), and so I obtained the period of a million years as the upper possible limit. In proportion as the percentage of ionium oxide present is less than 100 %, this period must be reduced.[*] Thus we have fixed the period of ionium as between 10^{-5} and 10^{-6} years, if ionium is the only intervening long-lived member.

Quite recently a method has been devised for calculating the period of ionium from the range of its α-particles, which is based upon an empirical mathematical relation holding between this range and the periods of the substances giving α-rays in the case of the other members of the series.[†] The most recent estimate by this method is about 200,000 years, which may be accepted provisionally as the most probable at the present time. If this is correct, there should be 25 grams of ionium per ton of uranium in minerals. A variety of evidence thus leads to the conclusion that to detect the growth of radium from uranium either still larger quantities of uranium or still longer time is necessary. Even after ten years, that is at the end of 1916, if the period of ionium is as estimated, the uranium in No. III preparation should only have produced 12×10^{-12} grm. of radium, which is less rather than half the amount that will then have been formed by the ionium initially present. Nos. I and II preparations are very much less favourable. But it is interesting to consider No. IV preparation, which, though only $2 \cdot 6$ years old, has over seven times as much uranium as No. III. From the present slope of the curve it appears to have little more than one-half as much ionium, relatively to the uranium as No. III, whereas the relative initial quantity of radium is about twice as great as in No. III. After eight years, that is in 1917, the quantity of radium produced from the uranium should be about equal to that which will have by then been produced from the ionium present. A distinct upward slope should be detectable in the growth curve some time before this. But this is the best, if the estimate of the period of ionium assumed

* Soddy, Le Radium, 1910, vii. 297.
† Geiger and Nuttall, Phil. Mag., 1911, xxiii. 613, 1912, xxiii. 489.

is correct, that the present set of experiments can offer to the solution of the problem. With the experience already gained, especially in dealing with large quantities of uranium and in the methods of measurements of the minutest quantities of radium, there should be no difficulty in obtaining and dealing with sufficient uranium, say 20 kilograms, of the requisite degree of purity as regards ionium and radium, to determine directly in a few years the period of ionium from the growth curve provided it is not greater than 200,000 years.

A favourable opportunity is being awaited to initiate this large-scale experiment. It requires a small room to itself in a permanent institution uncontaminated with radium, and some guarantee that once installed the preparations will remain undisturbed for a reasonable term of years, and that the measurements will be continued in a comparable manner should the period of life of the original investigator prove insufficient. It is not enough to set aside a quantity of uranium for our successors to see if any radium has grown in it. It is essential that the exact form of the growth curve should be known before the problem in question can be fully answered. There *may* be more than one long-lived intermediate product between uranium and radium. However, such indirect information as has been acquired as to the life period of ionium indicates that it, alone, is sufficient to account for the present results as regards the absence of growth of radium from uranium.

I desire to acknowledge my indebtedness to Mr. H. N. Beilby and Mr. George Weller for their expert advice and help in overcoming engineering difficulties encountered in the operation of the machine, and to Mr. A. H. Bodle, the mechanic of the Chemistry Department, for his skill and energy in constructing it.

[F. S.]

High Frequency Currents.

The subject of High Frequency Currents is an extremely fascinating
one, for not only are the effects obtained very beautiful, but also
there is an air of mystery about them which lends to their attractive-
ness. This mystery is in a large measure due to the fact that the
ordinary laws governing the flow of electric currents seem to be
violated, though on closer inspection this is not really the case.

The subject is now a very large one, and I propose to-night
merely to pass in review the different methods of generating high
frequency currents and to illustrate their principles experimentally.

Before proceeding it will be well that I should explain what I
mean by high frequency currents, and for this purpose I shall have to
rapidly survey a certain amount of elementary matter.

If an electric current flows continuously in the same direction
through a wire or other circuit, it is said to be a continuous or direct
current. If, however, the current flows along the wire first in one
direction, then in the other, alternately reversing its direction of flow,
it is said to be an alternating current. When the growth and decay
of the current and its reversal take place in a regular manner, we
speak of the number of times per second that the current goes
through a complete cycle of change as its frequency.

This is perhaps best illustrated by considering the motion of a
clock pendulum. The little pendulum which I am using to write
down its motion on the smoked glass in the lantern has a frequency
of two.

In the case of most alternating currents used for electric lighting
the frequency ranges between 50 and 100, and in the case of the
current supplied to this lecture theatre from Deptford the frequency
is 85. These might be thought to be high frequencies, but they are
really not at all high. The frequency of the current in the telephone
wires—say, for instance, when the electrophone is transmitting a high
musical note—might be as high as 1000. The upper limit at which
sounds appear to have a clearly musical character is probably of the
order of 10,000 per second, and the limit of audibility some 20,000
per second, depending on the individual.

It is possible to produce electric currents having frequencies ranging from 10,000 per second up to many millions, and it is currents between these frequencies that I call high frequency currents. This evening I am going to devote my attention more especially to frequencies in the range between ten thousand and a million, as currents of these frequencies have a large number of practical applications, such as wireless telegraphy, high frequency treatment of diseases, electrical cautery, thermo-penetration, etc.

The methods of producing high frequency currents may be divided broadly into three classes, namely : (1) Alternator methods ; (2) methods based on the oscillatory discharge of a Leyden jar ; (3) arc methods. Although the alternator method of producing very high frequencies has not had the same general application as the Leyden jar discharge, I will treat it first for two reasons : Firstly, it is some-

what easier to understand ; secondly, there seems a probability that the high frequency alternator will be very greatly improved and developed, and soon come into more general application.
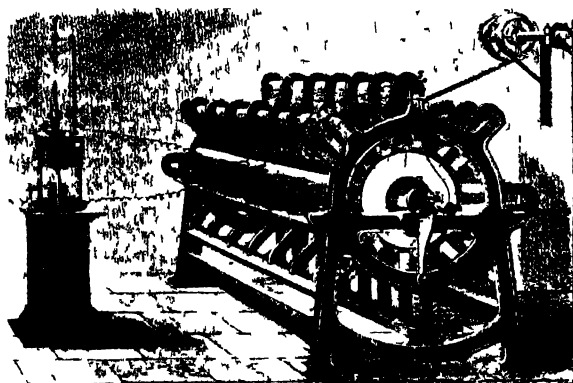
Alternators were among the first machines invented for producing electric currents on the well-known Faraday principle of magnetic induction. Among the early machines which will illustrate the principle I may mention the Alliance machine, which was largely used in lighthouses, from 1863 onwards. The essential parts were a number of magnets, and wires on bobbins which passed across the poles, in which electric currents were induced (Fig. 1). The frequency of these machines was about 50 per second.

Consider a single wire passing a north pole. A current will be induced in it in a certain direction, according to the well-known principles discovered by Faraday. When the wire passes across the

south pole a current will be produced in the opposite direction, so that we have here quite a simple means of producing a current which flows alternately in the wire in opposite directions—that is to say, an alternating current. If a number of magnets are arranged round the machine with their poles alternately north and south, and a wire is caused to move past them, an alternating current will be produced, the frequency depending upon the number of magnets and on the number of revolutions the machine makes per second. For instance, if we have 8 magnets, each of which has, of course, two poles, and if the machine makes 6 revolutions per second, then the frequency will be 48. It will be at once obvious that if we wish to generate a high frequency with a machine such as this, we can obtain it either by using a large number of magnets or a high speed of rotation, or both.

In a little special machine which I have here there are 15 magnets—that is to say, 30 poles alternately north and south—and it runs at 8000 revolutions per minute or 133⅓ revolutions per second, so that frequency in this case is 2000. The peripheral speed of this machine is just over 3 miles per minute—that is to say, the rotating part would roll down to Brighton in about 17 minutes. From this example it will be pretty obvious that if I attempt to obtain high frequencies—that is to say, frequencies well above 10,000—I shall have to run either at enormous speeds or have a very large number of poles. One of the very earliest high frequency machines ever constructed in this country, and following shortly after Tesla's high frequency machine, was made by Messrs. Pyke and Harris for Sir David Salomons, and owing to the courtesy of Messrs. Isenthal, who now own the machine, I am able to show it to you to-night.

The machine ran at 1500 revolutions per minute, but as both the armature and the field magnets are free to move, their relative rate was 3000 r.p.m. or 50 revolutions per second. The number of pairs of poles is 174, so that frequency is 8700.

This machine exhibits very well the peculiar difficulty there is in constructing high frequency alternators, for there are no less than 10 poles in each inch of the circumference of the discs which form the armature and field respectively. When it is remembered that it is not only necessary to get the 10 poles into 1 inch. but also the wires which are between them and the insulation on the wires, it becomes pretty obvious that the constructional difficulties are very great, especially if the machine is required to produce large currents, which naturally require large wires to carry them. As an example of an early machine, this machine possesses many points of interest. Firstly, the method adopted of revolving the two parts in opposite directions is extremely interesting, and has been followed in some of the modern machines. It enables twice the frequency to be obtained from the machine with the same risk of bursting the revolving parts as could be obtained if one part were stationary in the ordinary way and the other part revolved. Secondly, the method of winding—namely, the

zigzag winding of the wires on the poles—is of considerable interest. I believe it was first put into a high frequency machine by Tesla in 1889, and it has been adopted in many modern high frequency machines.

At about the same date that Sir David Salomons had his machine constructed, Mr. Parsons constructed for Prof. Ewing at Cambridge University a high frequency alternator in which the high frequency— namely, 14,000—was obtained by using a high speed of 12,000 r.p.m.

At this stage I would explain a second method of constructing an alternator which differs slightly in principle from the first. If, instead of moving the wires across the faces of the magnets, or moving the soft iron cores on which they are wound, the wires be wound on the poles of the magnets and a piece of soft iron moved past the magnet poles, an alternating current will be produced as before with this difference—each time the piece of soft iron bridges two poles and thus forms an easy path for the magnetism, the magnetism will increase through the coils producing a current in one direction, and as it moves away the magnetism will decrease and produce a current in the opposite direction. It will thus be evident that we produce a current first in one direction and then in the other as the piece of soft iron passes each individual pole instead of each pair of poles, so that for a given number of poles and a given speed this type of alternator will produce twice the frequency of the previous type. Alternators depending on this principle are usually called inductor alternators. Many high frequency alternators have been constructed on this principle by using 204 polar projections or teeth and a speed of 35,400 r.p.m. I have obtained a frequency of no less than 120,000 in a machine I constructed in the laboratories of the Central Technical College, but the output of the machine was microscopic.

It is of interest to consider what is the practical limit of frequency obtainable in alternators, and this entirely depends on the limiting speed from the point of view of safety at which the material may be run, and on the spacing of the poles. It is quite well known that for every material there is a limiting peripheral speed above which it will fail. With modern steels and good construction, the safe limit is somewhere in the neighbourhood of 300 metres per second. If we assume that we can get a pole and the wire and insulation into 3 mm., the total number of poles per second will be 100,000, and the limiting frequency would either be 100,000 or 50,000 according to whether the alternator was of the inductor or the ordinary type. If it were possible to build two discs rotating in opposite directions, having the above peripheral speeds, then the above frequencies would be doubled. The limited width available for the pole and copper leads to great difficulties if any considerable output is required.

Turning to modern high frequency machines, we have the alternator designed by Mr. Alexanderson, with which frequencies as high as 200,000 have been obtained. Owing to the courtesy of Mr. Alexanderson, I am
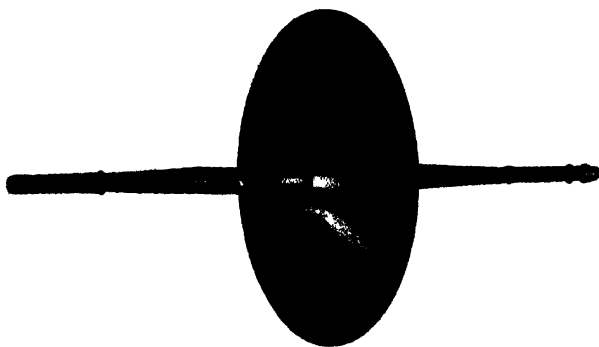
Fig 2 —Disc of Alexanderson's 100,000 ~ Alternator

Fig 3 —Disc of Alexanderson's 100,000 ~ Alternator

able to show you some photographs of a 100,000 frequency machine and give you some details as to its construction. The alternator is
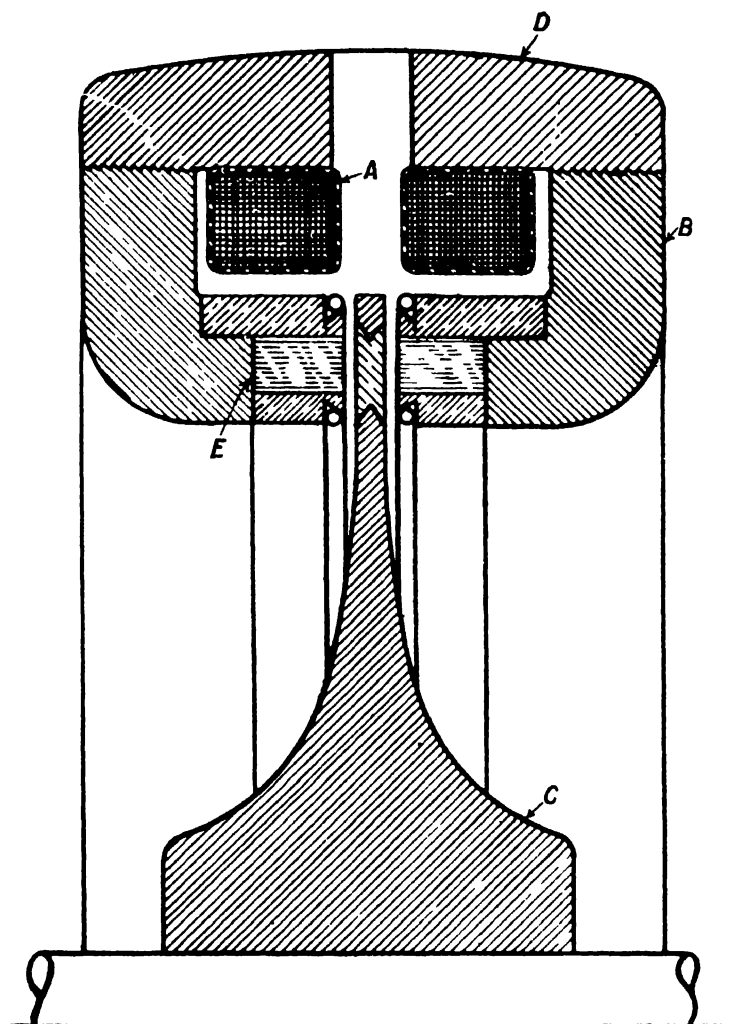
FIG. 4 —SECTION OF ALEXANDERSON'S 100,000 ∼ ALTERNATOR

of the inductor type. The rotating part consists of a steel disc having 300 slots cut round its edge so as to leave 300 steel teeth. Each of these steel teeth acts in turn to close the magnetic circuit between

two of the poles of the stationary part of the machine. In order to reduce the air friction on this disc, which is run at the very high speed of 20,000 r.p.m., the spaces between the teeth have brass plugs riveted into them so as to render the surface of the disc perfectly smooth. Fig. 2 shows the complete disc and its shaft, and Fig. 3 a portion of the disc on a larger scale.

The frame of the machine F, Fig. 4, contains two field coils A. The magnetic lines of force pass through the frame through the part B and the laminated polar projections E. According to whether there is an iron spoke or the non-magnetic material between the polar projection E, the magnetic flux will be maximum or minimum, and will consequently go through a complete cycle of change as each iron
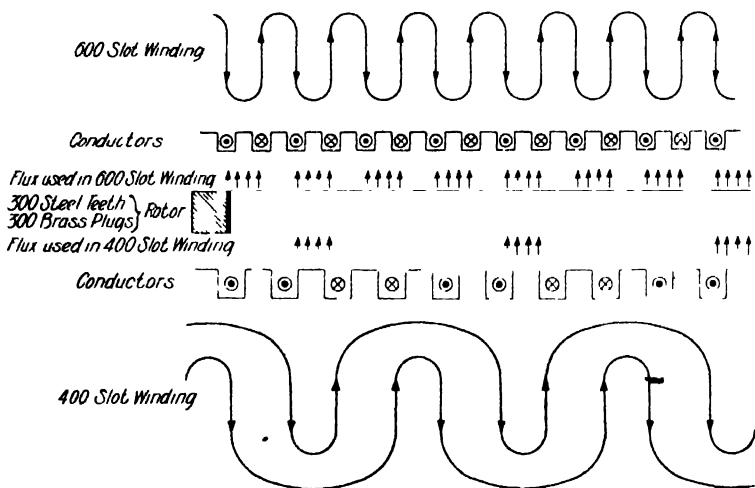
FIG 6.—WINDING DIAGRAM, ALEXANDERSON'S ALTERNATOR.

spoke passes the pole tips ; the wires in which the current is induced are wound zigzag fashion around the pole tips. With 300 teeth and a speed of 20,000 r.p.m., a frequency of 100,000 is obtainable. A view of the complete machine is shown in Fig. 5, the driving motor being on the right, the gearing in the centre and the high frequency alternator on the left. An output of some 2 k.w. is obtainable. In order to get still higher frequencies without rendering the spacing excessively small so that there is no room for the wires between the polar projections on the stator, another form of winding has been adopted in which instead of using 600 polar projections on the stator only 400 are used. This winding is illustrated in Fig. 6.

With this latter type of winding, using 800 polar projections, a
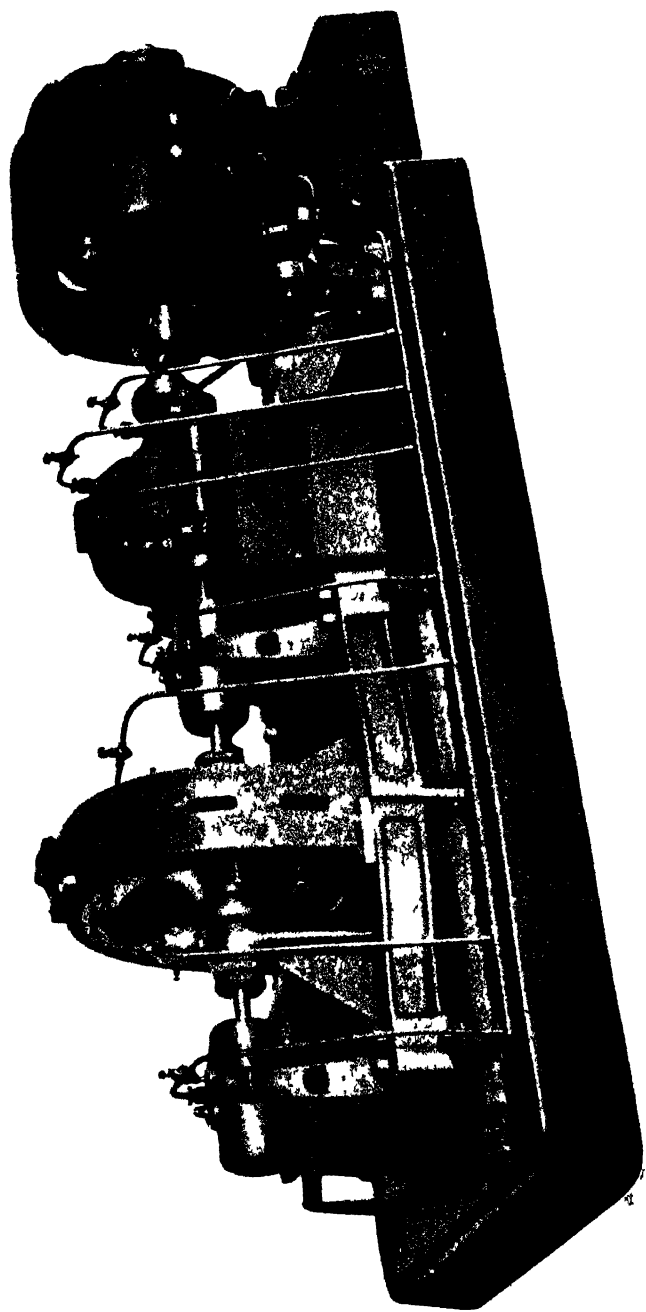
Fig 5

frequency of 200,000 has been obtained by Mr. Alexanderson. It is interesting to note that when running at this very high speed the gyrostatic action is so considerable that a long flexible shaft has to be used so that the disc spins in its own plane like a top. Auxiliary bearings are provided close to the disc, which, while allowing sufficient freedom for the disc to spin in its own plane, yet prevent excessive bending of the shaft when the disc passes through its different critical speeds when being speeded up. To give some idea of the high speeds at which these discs run I may mention that the speed of the edge is some 12 miles per minute, so that if they could be used as wheels for a motor car, the journey to Brighton would only occupy about $4\frac{1}{2}$ minutes.

A high frequency alternator on quite a different principle is due to Dr. Goldschmidt. The principle of the machine is at first sight a little difficult to understand. I have mentioned in Sir David Salomon's early machine that the two discs forming the field and armature were rotated in opposite directions. It is possible, however, to produce a rotating field electrically without the disc moving at all. When this is accomplished the frequency of the machine depends as before upon the relative speed of the rotating field and the armature.

Considering for simplicity a machine having only two poles so that it gives one complete cycle per revolution, and suppose I supply the fixed part or stator with an alternating current of 100 frequency and so connect it that it will produce a rotating field (we will assume the alternating current to be three phase for the sake of simplicity), if now I rotate the rotating part in the opposite direction to that of the rotating field I shall have induced in the rotor an alternating current whose frequency will depend on the relative speeds. For instance, if the speed of the rotor is such that with a stationary field it would give 100 frequency, then as my field is actually rotating in the opposite direction at 100 frequency the actual frequency produced will be 200 per second. Using this 200 per second frequency by means of another machine running at the same speed one could increase it to 300, and so on indefinitely. This would, however, lead to a very complicated machine, and Dr. Goldschmidt has arranged matters so that instead of requiring a number of machines the successive additions to the frequency can all go on in the same machine.

The simplest way to explain this is to suppose that the alternating current at 200 frequency obtained from the rotor is passed back into the stator of the same machine so as to produce a rotating field of 200 frequency without in any way interfering with the original rotating field of 100 frequency. This rotating field of 200 frequency will induce an alternating current of 300 frequency in the rotor, which could in turn be transferred back to the stator and produce a rotating field having 300 frequency, and so on.

This is what Dr. Goldschmidt calls the electrical method of trans-
ferring the currents from the rotor to the stator. He has also devised
a magnetic method which is simpler. Turning again to our two pole
machine whose stator is supplied with current at 100 frequency, there
will be induced in the rotor a current of 200 frequency. Now, if
the rotor be short-circuited there will be produced in it a rotating
field having 200 frequency, which will induce in the stator a current
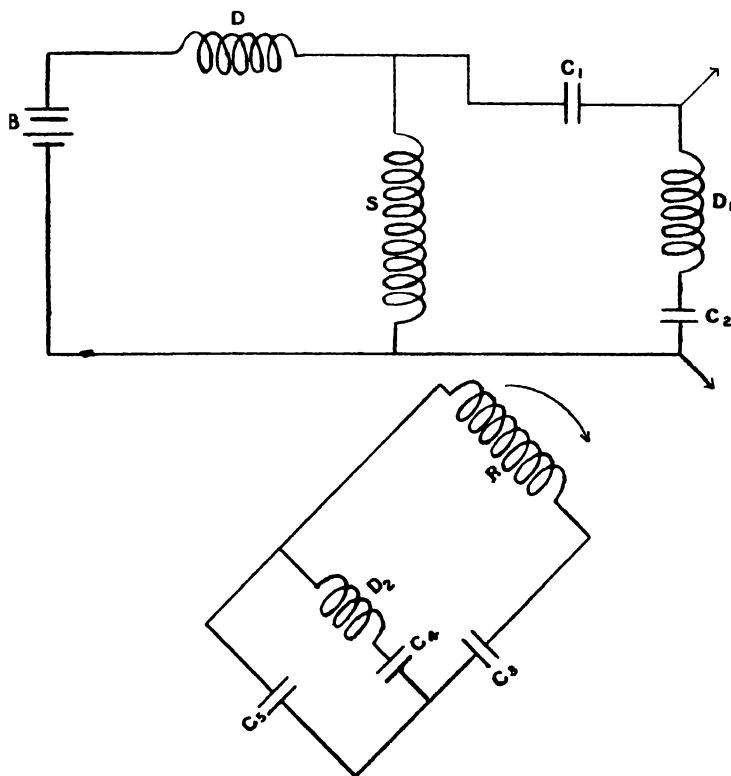
FIG 7 —GOLDSCHMIDT'S ALTERNATOR.

having 300 frequency, which in turn can be short-circuited and will
induce in the rotor a current having 400 frequency, and so on. I
have spoken of the machine as if the rotating field was produced
by a three phase current. A single phase field may be looked upon,
theoretically, as two rotating fields in opposite directions, one of
which will have no effect as far as we are concerned, and therefore a
single phase machine will do just as well. Further, it is not really

FIG. 8.--ROTOR OF GOLDSCHMIDT'S ALTERNATOR.
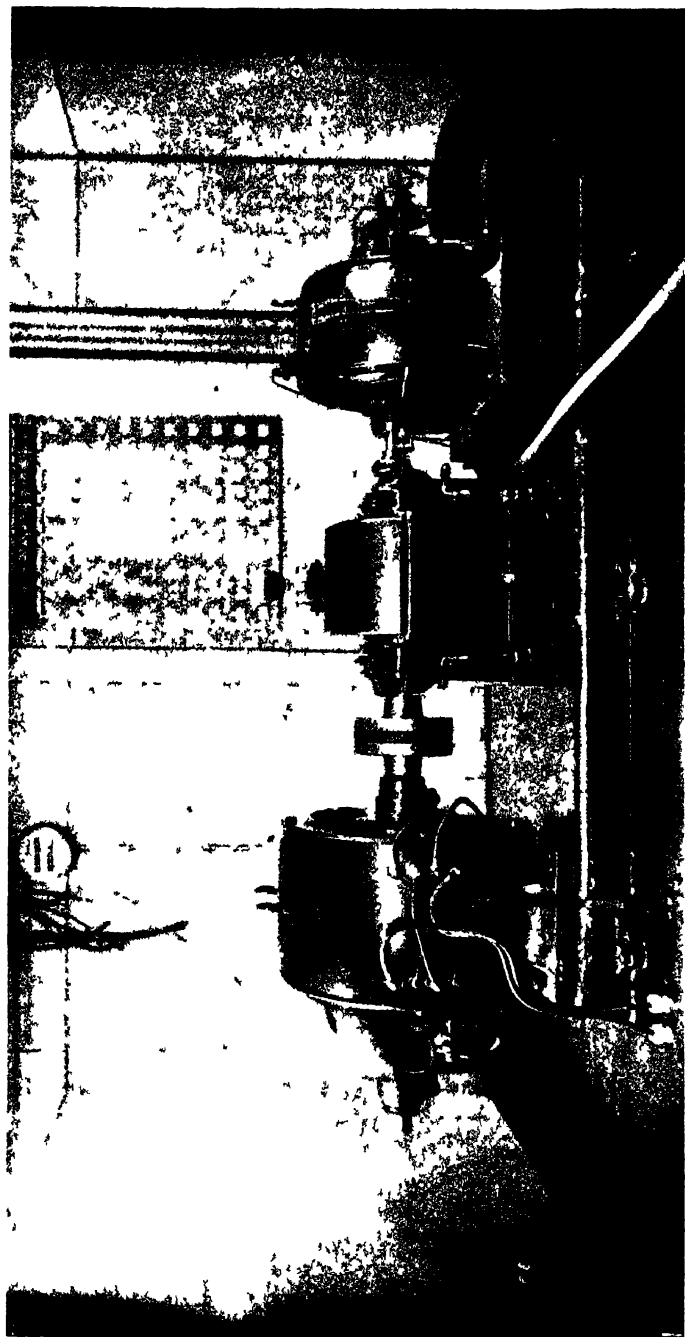
FIG. 9.—GOLDSCHMIDT'S ALTERNATOR COMPLETE.

necessary to supply the stator of the machine with an alternating current. If it is excited with a direct current it will induce an alternating current in the rotor which will react on the stator, and backwards and forwards in the same way as I have already described.

It would seem at first sight as if by this means an indefinitely high frequency could be very easily obtained. There are, however, certain practical difficulties. The actual connections used for a fourfold magnetification of frequency are shown in Fig. 7.

The stator S is excited from the battery B through the self-induction D. This produces in the rotor R an alternating current of the frequency of say 100. This current flows through the condenser C_3, the self-induction D_2, and the condenser C_4. This circuit being in resonance for 100 frequency, consequently the rotor behaves as if short-circuited for this frequency. The field produced by this 100 frequency will react on the stator, and induce in it a current of 200 frequency which passes via the condenser C_1, self-induction D_1, and condenser C_2. This circuit is also adjusted to be in resonance for the frequency 200, and consequently the stator behaves as if short-circuited for this frequency. There is in turn induced in the rotor R a current of 300 frequency which passes via C_3 and C_5, again adjusted to resonance. This induces in the stator a current of 400 frequency which, as circuit $D_1 C_2$ is not in resonance, for this frequency can be taken out to do useful work from the points a and b. By this method Dr. Goldschmidt has obtained some 12 k.w. at a frequency of 30,000, and at high frequencies a lesser output. Owing to his courtesy I am able to show you some slides of the actual machine. Fig. 8 is the rotor, and Fig. 9 the complete machine.

The present position of the generation of high frequency currents by means of alternators may be resumed by saying that it is now practically possible to generate by means of a machine alternating current up to and over 200,000 frequency. At frequencies of 100,000 several k.w. are obtainable, and at the lower frequencies machines can be built for greatly increased outputs. Where large amounts of power at high frequencies are required such as in wireless telegraphy, the question is now becoming a commercial one as to the efficiency of the different types of alternator, their cost and their reliability. Is it possible to run these machines continuously day in day out and to supply power at high frequencies? If so, how much does it cost per kilowatt hour to produce this high frequency power, taking into account not only the coal consumption, but also the wear and tear on the machine and all the other running and capital charges?

LEYDEN JAR DISCHARGES.

Turning next to the second method of producing high frequency currents—namely, by the discharge of a Leyden jar—it was quite early inferred by Helmholtz and Henry that the discharge of a Leyden jar

did not always flow in the same direction, and we owe to Lord Kelvin the mathematical investigation of this subject, and to Feddersen its experimental demonstration. If I charge a Leyden jar, or any other condenser, and allow it to discharge through a very high resistance, a current will flow, which gradually dies away as the jar discharges. If, however, I discharge the condenser through a sufficiently low resistance, it will be found that the current continues to flow in the same direction after the jar is completely discharged, and then charges it up in the opposite direction, the current gradually getting smaller. When the jar is charged to a certain extent in the opposite direction to its original direction it starts to discharge again, this time in the opposite direction. The current again continues to flow after the jar is discharged, and charges it up in the original direction. This cycle of operation is repeated, the energy of the charge in the jar gradually getting less and less, until it dies away. As a simple analogy, a pendulum, or a weight hanging on a spring, when displaced oscillates, the oscillations growing smaller and smaller until they die away. This is so well known that I need not go any further into the matter. The frequency of these oscillations is determined by the capacity of the condenser—that is to say, the quantity of electricity it can hold when charged to 1 volt and the self-induction of the circuit—the capacity of the condenser corresponding to the weakness of the spring, and the self-induction to the mass of the weight in our spring and weight analogy.

It is quite easy to obtain by this method almost any frequency— for instance, anything between 1 and 100,000,000 are comparatively easily obtainable, and I have even demonstrated frequencies as low as $\frac{1}{2}$ in this lecture theatre.

The fundamental difference between these high frequency currents and those generated by alternators is that they die away—that is to say, that the amplitude gradually decreases and comes to zero. The condenser then has to be re-charged, and the process repeats itself. Now, a single discharge of this sort is not of much practical use. It is necessary to charge the condenser and repeat the discharges in rapid succession if any useful work is to be done. Many methods have been proposed for this purpose. Some of the early successful experiments were those of Tesla, shown in this theatre on February 3, 1892.

The condenser is allowed to discharge through a circuit which consists of the necessary self-induction and a spark gap in series. Now, a spark gap possesses the property of acting like a safety valve which will stand a certain steam-pressure, and will then suddenly open and let the steam out freely. The spark gap will stand a certain electrical pressure, and then will open and let the electricity pass. When once the electrical pressure or voltage has been raised to a sufficiently high value to break down the spark gap, the spark gap changes from being an insulator which prevented the flow of electricity

to being a comparatively good conductor, and it remains conducting in the ordinary way until the current finally ceases. I shall have some more to say later on the subject of the change of conductivity of the spark gap. Returning to our circuit containing our condenser, spark gap and self-induction, if the condenser be charged to a sufficiently high voltage the spark gap will break down, a spark will take place, and during the time that the gap is conducting oscillations will take place. In order, therefore, to produce the repeated sets of discharges of the condenser, all we have to do is to repeatedly charge the condenser to a sufficiently high voltage, and this is easily accomplished by charging it from a transformer connected to an ordinary low frequency alternator. For instance, with the ordinary 85 frequency current available I can obtain one discharge each time the condenser is charged either positively or negatively—that is to say, 170 discharges per second, each of which discharges consists of a series of high frequency oscillations.

This is the usual method of producing high frequency currents, and is the method used by Tesla for his most brilliant experiments, shown in this lecture theatre twenty years ago. It will be evident, however, that the high frequency currents obtained by this means differ fundamentally from those obtained from an alternator ; for instance, with an oscillation frequency of 1,000,000 per second, such as I am using, and 50 oscillations for each discharge of the jar, the whole discharge will last $\frac{1}{20000}$ of a second. As we are only obtaining 170 discharges per second, there is something like a 200th of a second between the end of one discharge and the beginning of the next, which is a comparatively long time, about 100 times as long as the time the oscillations last. Inventors have been struggling, and with some success, to close up these gaps.

It is obvious that if the discharges can be caused to take place with greater rapidity by using a higher frequency alternator to charge the jars, the gaps will be closed up, and this is the method originally used by Tesla, and which is now being used in many of the wireless transmitters, though in this case there is another reason for using a greater number of discharges per second. For instance, the Marconi Company, in their musical spark transmitters, use a frequency of some 300—that is to say, some 600 discharges per second—and the Telefunken Company as many as 1,000 discharges per second.

Mr. Marconi has described in this lecture theatre the method he uses in his trans-Atlantic stations. In this case, instead of charging the Leyden jar or condenser from an alternator, it is charged from a high voltage battery, and the sequence of discharges is produced by means of a special form of spark discharger, which consists of a disc fitted with studs round its edge. When this disc is rotated the studs pass between the balls of the spark gap, and, corresponding to the passage of each stud, a discharge takes place. If the disc is driven at a very high speed a large number of discharges per second

are obtainable. Taking the trans-Atlantic case, where the frequency of the oscillations is about 50,000 per second, and, assuming that there are 50 or 60 oscillations in the aerial for each discharge, the total time the oscillations in the aerial last is just over $\frac{1}{1000}$th of a second. As the spark frequency is about 600 per second the oscillations are therefore practically joined up, and there are no completely idle intervals between them.

I now come to another class of method which still depends upon the discharge of a condenser. If I have a body like a pendulum or a spring capable of oscillations, I can make it oscillate by pulling it away from its position of rest and then letting it go. I can also make it oscillate by giving it a blow or shock, and I can make it oscillate by applying to it a number of impulses at properly timed intervals. All three of these methods are employed in the production of high frequency currents. The first is the simple discharge of the Leyden jar without any auxiliary apparatus ; the third is the method usually employed in wireless telegraphy for obtaining and maintaining a long series of oscillations in the aerial by tuning it and loosely coupling it to the Leyden jar circuit in which the discharge takes place. The second method also involves a discharge of a condenser. In this case the spark gap is so arranged that it suppresses the oscillations of the condenser—that is to say, it breaks down, allows a large rush of current, and then becomes insulating and stops anything further from happening. To illustrate this I have constructed a little valve which works with water A vertical tube of water represents the condenser, and this is connected to the valve. The height of the water in the tube is gently increased, which corresponds to increasing the quantity of electricity in the condenser, and the pressure of the water, represented by its height, corresponds to the voltage on the condenser. When the pressure of water is sufficient the valve suddenly opens, corresponding to the spark gap breaking down, and allows the water to flow out from the vertical tube, so discharging it. As the valve only works in one direction oscillations cannot take place. We have thus a model of what is called a quenched spark, which goes out directly the condenser is discharged. A discharge of this type can be caused to act either by magnetic induction or otherwise on a circuit consisting of a condenser and a self-induction. The effect of the rush of current when the jar discharges is to give the second circuit a shock and set up oscillations in it.

It might be thought at first that in this method of producing oscillations there was no relationship between the nature of the swing in the first, or discharge, circuit and the frequency of the oscillations in the second circuit. Without going into the theory of coupling, which would take me too far, I would point out that for the best result there is a relationship, and this can be easily seen if one considers the question of starting oscillations in, say, a short and a long

pendulum. The long pendulum will be set swinging easier with a blow which comes on and off comparatively slowly, whereas the short pendulum will require a short, quick tap to start it swinging.

This method of shock excitation, due to Max Wien, is employed by the Telefunken Company in their wireless transmitter, and also in their therapeutic apparatus ; a special type of spark gap being used consisting of large flat metal plates, a very short distance apart, the object being to suddenly cool the spark to cause it to go out, and the gap to become insulating again at the earliest possible moment.

A spark gap of this type connected to a condenser and self-induction can be supplied in the ordinary way, when the frequency of the spark will naturally depend upon the frequency of the alternator.

If a Leyden jar or condenser be charged from a battery through a high resistance, it will take a certain time to charge up ; and if there be also connected to the condenser a discharge circuit containing a spark gap, when the condenser is sufficiently charged a discharge will take place through the spark gap, the condenser will then start to charge again and the operation will be repeated. I employed this method some years ago to work an induction coil. In this case, as I was only using low voltages under 1000 volts, the spark gap was replaced by a vacuum tube, and the self-induction in the oscillatory circuit was the primary of an induction coil. The connections and data are shown in Fig. 10. By suitably adjusting the pressure in the vacuum tube and the resistance in series with the condenser, it is easy to obtain a rapid series of sparks. If voltages of the order of 1000 volts direct current were generally available, this might form a very convenient method of working a coil.

It will be noted that the spark frequency is not, in this case, determined by an alternator, but depends upon the time the condenser takes to charge to a sufficiently high voltage to break down the spark gap. By making the resistance small, and the supply voltage high, the condenser will charge more quickly. It is quite easy to cause the discharges to follow one another very rapidly by this means.

If an attempt be made to employ the successive discharges of a condenser when charged from continuous current, a difficulty is encountered if large powers are dealt with. This difficulty seems to reside in the properties of the spark gap, which tends to become completely conducting, or, what is technically called "arcs," when large powers, say 10 k.w. or over, are employed.

Mr. Galletti set himself to get over this difficulty by employing a number of such circuits, each with their own spark gap, and connecting these together so that they would all help to produce the oscillations.

Of the methods proposed by him I will only refer to one which I have seen in operation. The principle of it is illustrated in Fig. 11. It consists of splitting the condenser into two parts, one of which— C_0—is common to all the discharge circuits. The action of this

condenser is not very easy to follow, but it certainly produces the required result, if the conditions are properly adjusted, by causing the discharges in the various circuits to take place in regular sequence. For it is quite easy to show that if the common condenser is not employed, then the circuits tend to all discharge at the same time, so that the addition of extra circuits, instead of filling up the gaps between the discharges, tends to accentuate the discharge, at certain
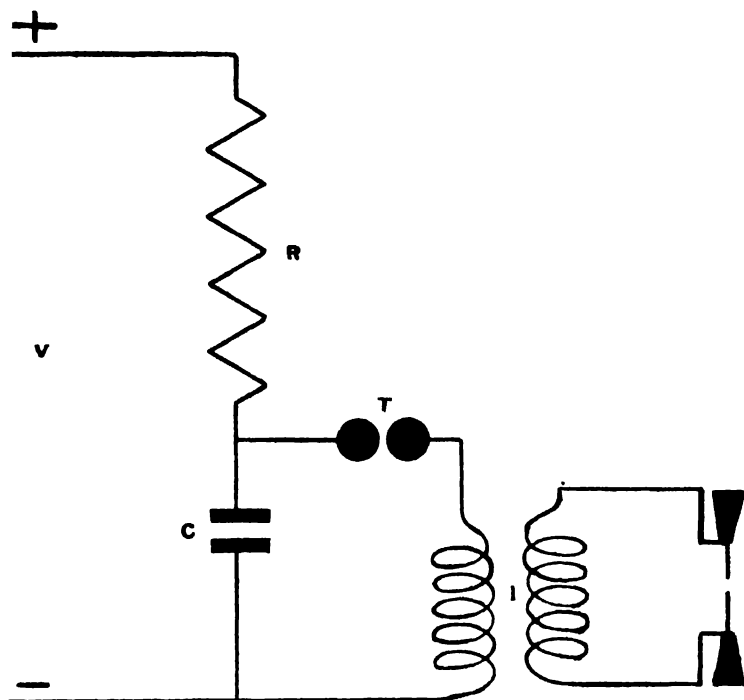
Fig. 10.

I, induction coil; T, vacuum tube, V, about 900 volts;
R, 5000 to 100,000 ohms; C, about 5 mf.

times leaving the intermediate periods idle. By combining a number of circuits and using the high voltage continuous current supplied by the Moutier-Lyons transmission—which was at a voltage of some 40,000 volts when I saw the experiments—Mr. Galletti was able to deal with many k.w., the spark frequency being very high, some 10,000 per second. Corresponding to each of these sparks there is a series of oscillations, so that in this case the oscillations must be
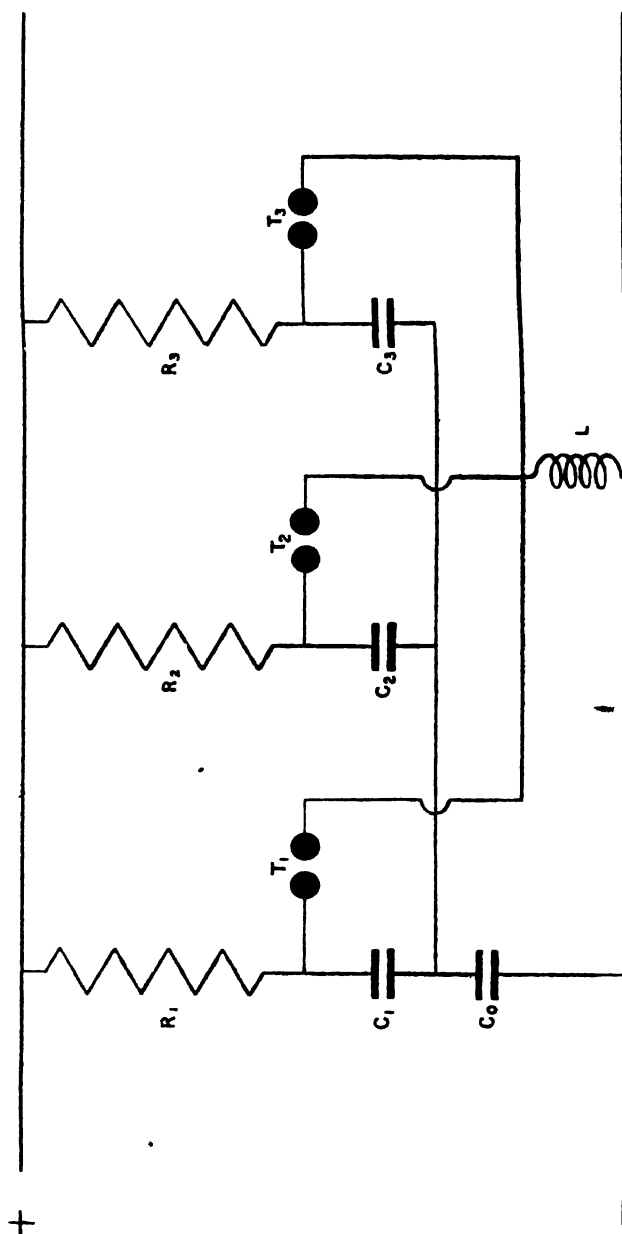
FIG 11—GALLETTI CONNECTIONS

completely joined up, and the result almost the same as if an alternator were employed.

Mr. Galletti informs me that he has been able to employ still larger numbers of sparks per second, up to 100,000. In this case one arrives at the interesting result that the oscillations can be maintained by impulses from the condenser circuit every other oscillation, or even each individual oscillation. This should maintain a true alternating current, such as is produced by an alternator, with no waste intervals.

To experimentally illustrate the principle, I have arranged two circuits according to Mr. Galletti's method. As I have not at my disposal a very high voltage—in fact, I have only 900 volts—I am using vacuum tubes T_1 T_2 in place of the spark gaps, as by adjusting the pressure I can make them discharge regularly at these low voltages.

In order to demonstrate that the two circuits I am using really discharge in regular sequence and not simultaneously, I am using a low discharge frequency of about 1 per second. This is obtained by giving the condensers C_0 C_1 C_2 each a capacity of about 5 mf., and using 100,000 ohms for R_1 and R_2 in series in each circuit. By short-circuiting the common condenser C_0 the sequence of successive discharges is at once destroyed, and the condensers of the two circuits tend to discharge simultaneously. When I reduce the series resistances the discharge rate is greatly increased, until it is no longer possible by eye or ear to realize the frequency. I have, by experiments with the oscillograph, determined that the discharges still take place in regular sequence.

ARC METHODS.

I now come to the third method—namely, the arc method of producing high frequency currents. If an ordinary direct current arc is produced between solid carbon or metal electrodes, it is unstable - that is to say, it cannot be burnt unless a resistance is placed in series with it. The reason for this will be at once evident if we examine the curves in Fig 12, connecting the potential difference and the current. It will be noted that if the current through the arc is increased, due to any cause, the potential difference between its terminals decreases. The result of this decrease in potential difference is to encourage a still larger current to flow. This larger current further decreases the potential difference, and, consequently, still further increases the current, the current tending, therefore, to become infinitely great. If, on the other hand, the current be decreased, the potential difference between the terminals of the arc tends to increase, which has the result of tending to still further decrease the current, causing the current to become zero, so that an
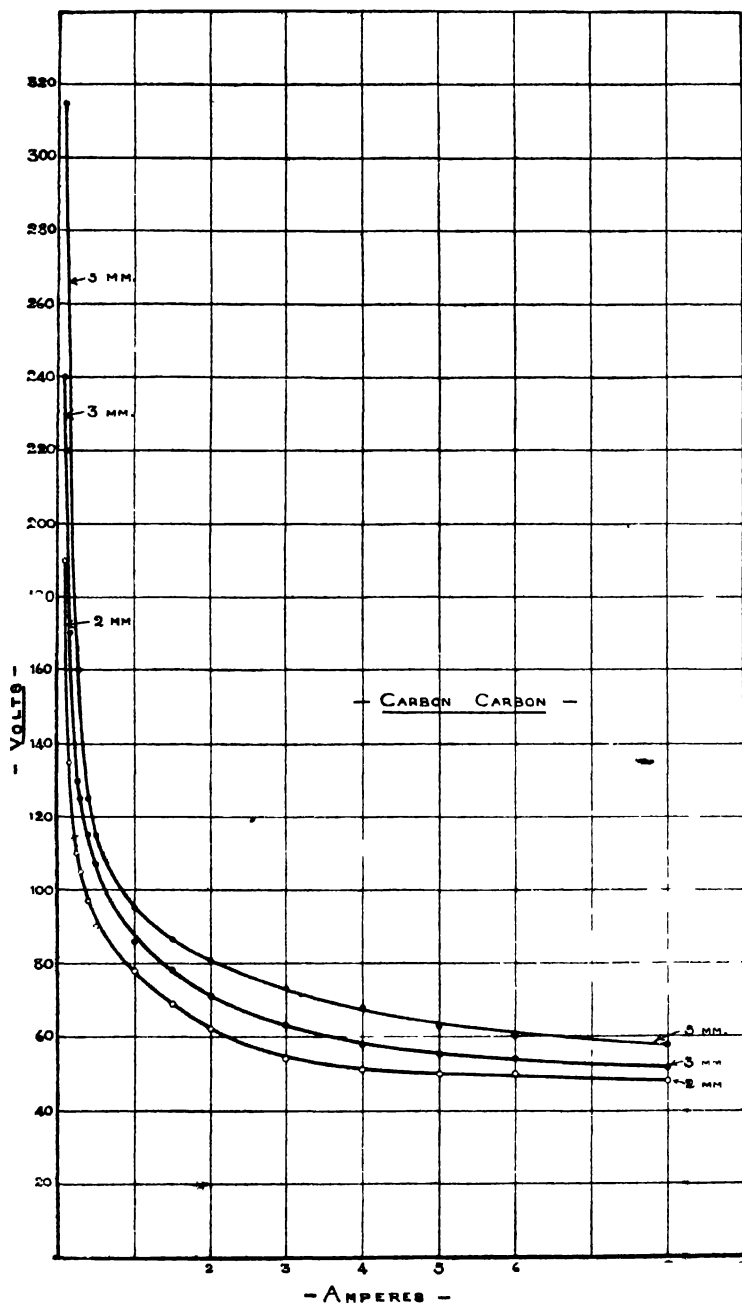
Fig. 12.—Characteristic Curves for Arc between Carbon Electrodes.

arc by itself is essentially unstable. Of course, in practice, the current can be kept at any desired value by putting sufficient resistance in series with the arc, so that when the current is increased the potential difference between the terminals of the arc and the resistance taken together increases, and the circuit as a whole becomes stable. If such an arc be shunted with a capacity and self-induction in series (see Fig. 13) oscillations will be set up in this shunt circuit, the frequency of the oscillations being mainly determined by the periodic time of the shunt condenser circuit, which may be calculated from the well-known Kelvin formula.

When the oscillations are taking place the oscillatory current flows through the arc, and consequently tends to increase and decrease the arc current. Any increase in the current tends to make the vapour column of the arc larger, and any decrease makes it
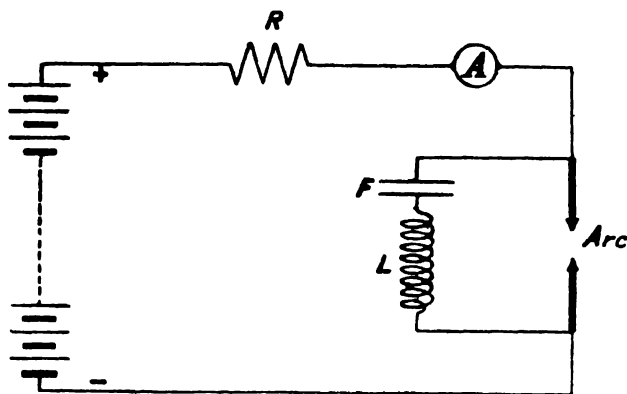
FIG. 13.- MUSICAL ARC CONNECTIONS

smaller, so that the vapour column of the arc pulsates in size. This pulsation in the size of the vapour column moves the air in the neighbourhood of the arc, and, if the frequency is suitable, produces sound ; hence this experiment is known as the musical arc. By varying either the capacity or the self-induction the frequency of the oscillations can be varied, and hence the pitch of the notes given out by the arc, and by this means a tune can even be played on it.

The frequency of the currents produced when using an ordinary arc between solid carbon electrodes is comparatively low, at the most a few thousands per second. The reason for this is that the characteristic of the arc—that is to say, the relationship between the potential difference and the current—depends to some extent on how quickly the current is varied. If the current is varied very quickly, then an increase of current is accompanied by an increase in the
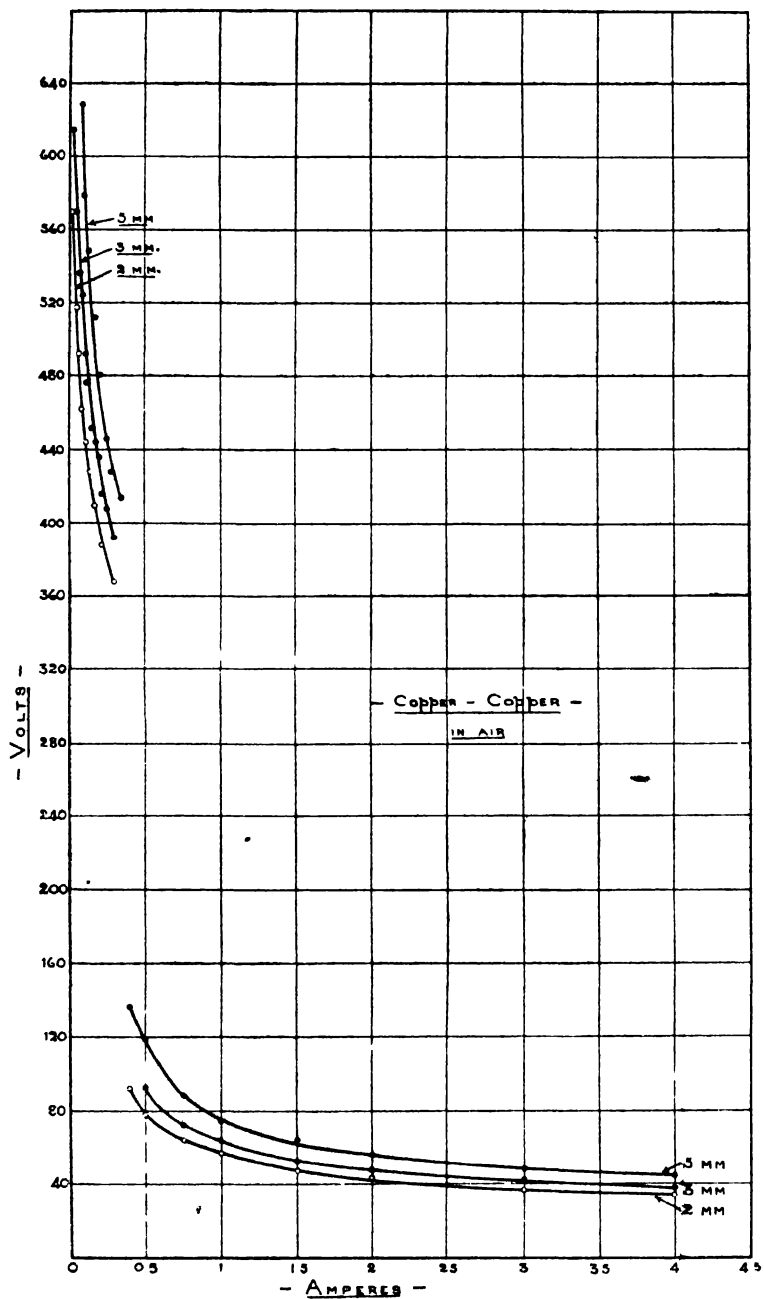
Fig. 14 —Characteristic Curves for Arc between Copper Electrodes.

potential difference ; the arc is no longer an unstable conductor, and oscillations cannot be produced.

There are various ways of rendering the arc unstable, even when the current varies rapidly. One of these consists in using very small currents. For instance, metal arcs using currents under one-half of an ampere are extremely unstable, and remain so even under high frequencies (see Figs. 12 and 14, which give some curves I have obtained for arcs between carbon and copper electrodes respectively).

Another method is to energetically cool the electrodes ; for instance, to make one of the electrodes consist of a vessel containing water, or squirt a jet of water through the arc. The third method, due to Mr. Poulsen, consists in placing the arc in hydrogen, or some hydrogen compound, such as coal-gas or alcohol vapour. By this means high frequency oscillations can easily be produced up to about a million per second, and at the lower frequencies of, say, 100,000, considerable powers can be dealt with.
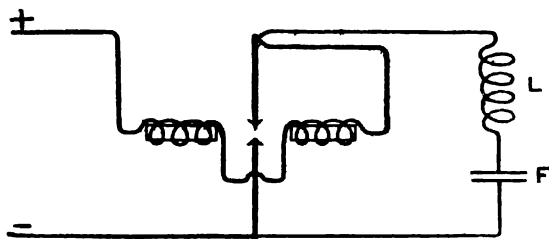
FIG 15 —POULSEN ARC CONNECTIONS.

To render the arc still more unstable, Mr. Poulsen places it in a strong transverse magnetic field (Fig. 15). With an apparatus of this sort I am informed that some 30 k.w. or more can be dealt with by a single arc, and if several arcs are placed in series large powers can be transformed. Fig. 16 is a photograph of a 12 k.w. arc generator.

If the apparatus is properly adjusted the high frequency currents produced are very nearly true alternating currents, such as are obtained from an alternator.

The only difficulty I find in working the apparatus is to maintain the frequency absolutely constant, as it appears that the frequency depends to a small extent on the current through the arc and on the arc length. In the actual apparatus employed for wireless telegraphy the electrodes are kept in rotation so as to ensure a greater constancy in the arc length.

It must be remembered that if the arc is burnt in coal-gas instead of the electrodes burning away, carbon is actually deposited, and the carbon electrode increases in length.
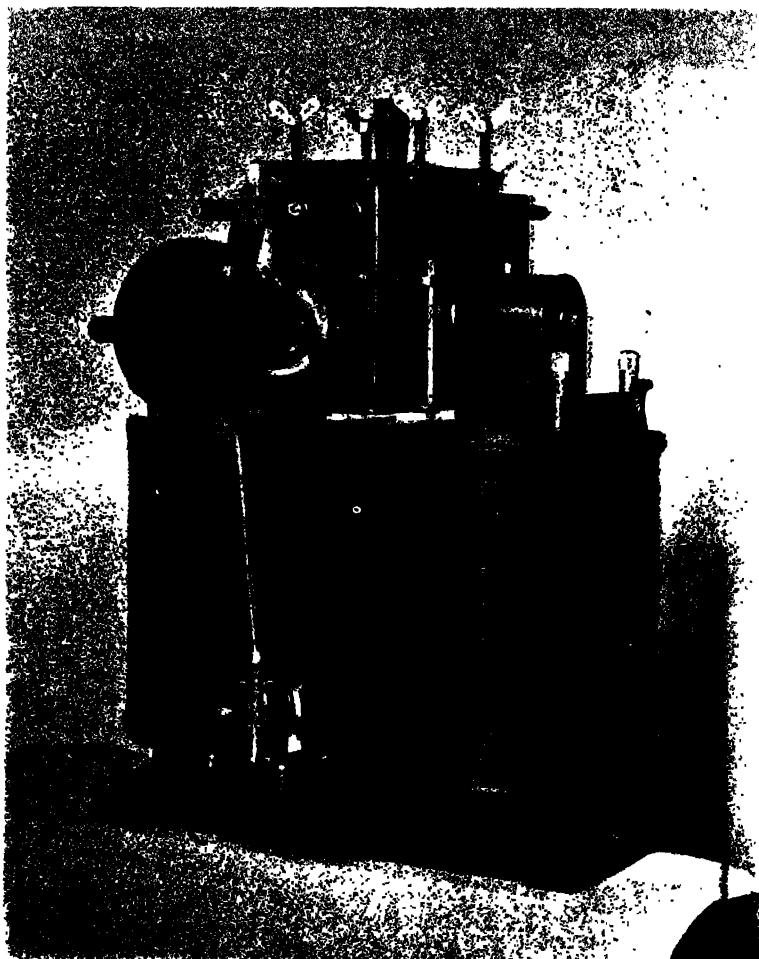
FIG. 16.—12 K.W. ARC GENERATOR.

In using a generator of this sort for wireless telegraphy, messages have been transmitted and recorded from a distance of about 1000 miles at the speed of over 100 words per minute.

A large number of modifications of the arc method have been produced, practically all of which consist in changing the nature of the electrodes or the surroundings of the arc, so as to try and make it still more unstable at high frequencies and large currents. Most arcs seem to lose their instability after the current has passed a certain limit. For this reason there is generally a best working current for any arc. If it is required to deal with more power than one arc can transform, it is better to put the arcs in series.

A trick which is very useful and which enables two arcs to be burnt in parallel as far as the mains are concerned, and to be in series as far as the oscillatory circuit is concerned, is illustrated in Fig. 17. This is at times very convenient, as sufficiently high voltage direct current generators are not always available.
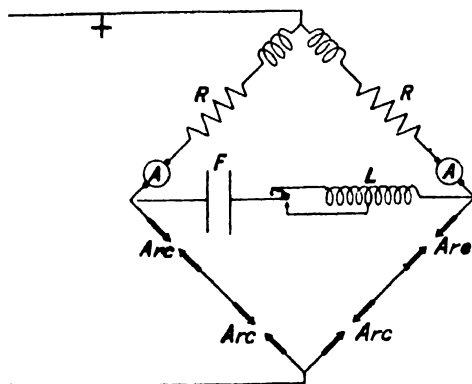
FIG. 17.—CONNECTIONS FOR ARCS IN SERIES PARALLEL.

A very interesting generator of high frequency currents is that invented by Mr. S. G. Brown. It is difficult to say whether it is an arc or a spark or what. The unstable conductor which takes the place of the arc consists of an aluminium wheel, on the edge of which a copper block rests (Fig. 18). The wheel is kept rotating, and the contact is shunted by a condenser and self-induction. This arrangement produces high frequency currents quite easily, but I have never been able to make it deal with any large powers.

In conclusion, it is of interest to review in general terms the present position of the three main methods of producing high frequency currents. The most important application at the moment for high frequency currents is wireless telegraphy. For this purpose frequencies in the range between 30,000 and 1,000,000 are required. A few

kilowatts high frequency energy is generally sufficient for practical purposes at the higher frequencies. At the lower frequencies, which are mainly used on long-distance working, large amounts of power are required. In fact one of the great problems in long-distance wireless telegraphy is to produce several hundred kilowatts of high frequency energy with certainty and regularity, and at a reasonable price.

The relative advantages of high frequency alternating current, sometimes called continuous oscillations and groups of oscillations, is not a matter that I can enter into to-night. It is sufficient to point out that if continuous oscillations are employed they can always be cut up into groups by means of an automatic device should this be required. Neglecting the relative advantages of the continuous oscillations and the oscillations which are sent out in groups with spaces between, I have simply to compare the three methods from the point of view of the amount of energy they are able to successfully and regularly handle.
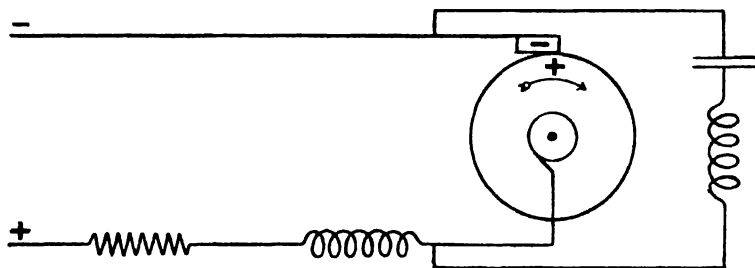
Fig. 18.—Connections for S. G. Brown's Wheel.

The alternator method, as far as the information at my disposal goes, has never yet been applied to very large powers. There is no doubt that it is from many points of view an ideal method.

The spark method has been successfully employed over a wide range of frequency and up to very large powers, and there is no doubt that it is capable of satisfactory operation. The spark method used with very high frequency sparks and continuous current, as proposed by Mr. Galletti, is still in its experimental stage. With the rough apparatus I saw working a year ago, a considerable amount of power could be dealt with successfully, and there seems no reason why the principle should not be extended so as to deal with still larger powers. The practical difficulties may be great, but I think they should be able to be overcome. This, however, is entirely a matter for experiment.

The arc method is in a much more advanced condition. A large amount of work has been done, and practically all the details have been worked out. There is no doubt that fairly large powers can be successfully generated and utilized.

The position is therefore a very interesting one. No one of the methods seems at the moment to have so many advantages as to make it *the* one method above all others for producing high frequency currents. The final decision as to which is the best will probably in the end be determined by the regularity with which the apparatus works, and by that governing factor in all commercial enterprises— the cost of production.

[W. D.]

Friday, January 17, 1913.

His Grace The Duke of Northumberland, K.G. P.C. D.C.L.
F.R.S., President, in the Chair.

Professor Sir J. J. Thomson, O.M. LL.D. D.Sc. F.R.S. M.R.I.,
Professor of Natural Philosophy, Royal Institution.

Some Further Applications of the Method of
Positive Rays.

THE method to which I shall refer this evening is the one I described
in a lecture I gave here two years ago. The nature of the method
may be understood from the diagram given in Fig. 1. A is a vessel
containing the gases at a very low pressure ; an electric discharge is
sent through these gases, passing from the anode to the cathode C.
The positively electrified particles move with great velocity to-
wards the cathode ; some of them pass through a small hole in the
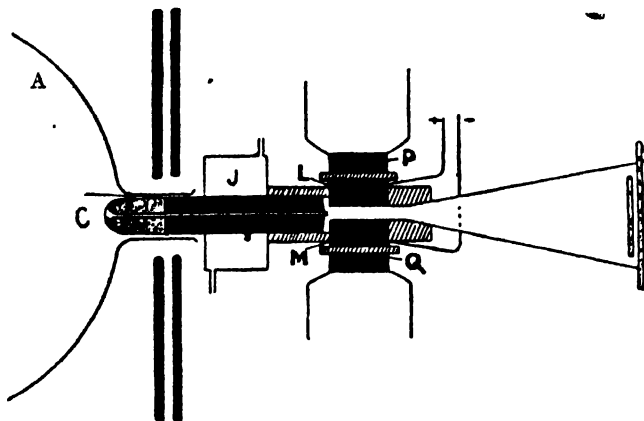
Fig. 1.

centre, and emerge on the other side as a fine pencil of positively
electrified particles. This pencil is acted on by electric forces when
it passes between the plates L and M, which are connected with the

terminals of a battery of storage cells, and by a magnetic force when it passes between P and Q, which are the poles of an electro-magnet. In the pencil before it passed under the influence of these forces there might be many kinds of atoms or molecules, some heavy, others light, some moving quickly, others comparatively slowly, but these would all be mixed up together. When they are acted on by the electric and magnetic forces, however, they get sorted out, and instead of travelling along the same path they branch off into different directions. No two particles will travel along the same path unless they have the same mass as well as the same velocity ; so that if we know the path of the particle we can determine both its mass and its velocity. In chemical analyses we are concerned more with the mass than with the velocity, and we naturally ask what is the connexion between the paths of particles which have the same mass but which move with different velocities. The answer is that all such paths lie on the surface of a cone, and that each kind of particle has its own cone ; there is one cone for hydrogen, another for oxygen, and so on. Thus one cone is sacred to hydrogen, and if it exists there must be hydrogen in the vessel ; so that if we can detect the different cones produced from the original pencil, we know at once the gases that are in the tube. Now, there are several ways of identifying these cones, but I shall only refer to the one I have used in the experiments I wish to bring before you this evening. These moving electrified particles, when they strike against a photographic plate, make an impression on the plate, and a record of the place where they struck the plate can be obtained. Thus, when a plate is placed in the way of the particles streaming along these cones, the sections of these cones by the plate (parabolas) are recorded on the photograph, hence we can identify these cones by the parabolic curves recorded on the photograph, and these parabolas will tell us what gases are in the vessel.

The first application of the method which I shall bring before you this evening is to detect the rare gases in the atmosphere. Sir James Dewar kindly supplied me with two samples of gases obtained from the residues of liquid air ; the samples had been treated so that one might be expected to contain the heavier gases, the other the lighter ones. I will take the heavier gases first. The photograph for these is shown in Fig. 2. When the plate is measured up it shows a faint line corresponding to the atomic weight 128 (xenon) ; a very strong line corresponding to the atomic weight 82 (krypton), a strong argon line 40 (argon), and the neon line 20. There are no lines unaccounted for, and hence we may conclude that in the atmosphere there are no unknown gases of large atomic weight occurring in quantities comparable with those of xenon or krypton. This result gives an example of the convenience of the method, for a single photograph of the positive rays reveals at a glance the gases

in the tube. I now turn to the photograph of the lighter constituents shown in Fig. 3 ; here we find the lines of helium, of neon (very strong), of argon, and in addition there is a line corresponding to an atomic weight 22, which cannot be identified with the line due to any known gas. I thought at first that this line, since its atomic weight is one-half that of CO_2, must be due to a carbonic acid molecule with a double charge of electricity, and on some of the plates a faint line at 44 could be detected. On passing the gas slowly through tubes immersed in liquid air the line at 44 completely disappeared, while the brightness of the one at 22 was not affected.

The origin of this line presents many points of interest; there are no known gaseous compounds of any of the recognized elements which have this molecular weight. Again, if we accept Mendeleef's Periodic Law, there is no room for a new element with this atomic weight. The fact that this line is bright in the sample when the neon line is extraordinarily bright, and invisible in the other when the neon is comparatively feeble, suggests that it may possibly be a compound of neon and hydrogen, NeH_2, though no direct evidence of the combination of these inert gases has hitherto been found. I have two photographs of the discharge through helium in which there is a strong line, 6, which could be explained by the compound HeH_2, but, as I have never again been able to get these lines, I do not wish to lay much stress on this point. There is, however, the possibility that we may be interpreting Mendeleef's law too rigidly, and that in the neighbourhood of the atomic weight of neon there may be a group of two or more elements with similar properties, just as in another part of the table we have the group iron, nickel, and cobalt From the relative intensities of the 22 line and the neon line we may conclude that the quantity of the gas giving the 22 line is only a small fraction of the quantity of neon.

Let me direct your attention again to the photograph of the heavier gases in the atmosphere. You will notice that the parabolas corresponding to many of the elements start from points which are all in the same vertical line ; this indicates that the atoms or molecules which form these parabolas all carry the same charge. Several of these lines, however, do not follow this rule ; you will notice, for example, that the neon line has a prolongation which comes nearer than the normal line to the vertical line drawn through the undeflected spot. Measurement of the photograph shows that the neon line begins at a distance from this vertical line which is only half the normal distance ; this shows that some of the neon atoms in the positive rings possess two charges of electricity ; the majority of them, however, only possess one. If you examine the argon line you will find that it comes even nearer to the vertical than the neon line : in fact, it begins at a distance from the vertical only one-third of the

normal distance ; this proves that the argon atom can have as many as three charges of electricity. If now you examine the krypton line you will find that it comes nearer to the vertical line than even the argon ; its least distance is one-fourth of the normal distance, showing that the krypton atom may have as many as four charges. The mercury line comes so close to the vertical line that it is only on large photographs that it can be seen that there is in reality an interval ; this interval is only one-eighth of the normal interval, showing that mercury may acquire eight positive charges, i.e. that it may lose eight corpuscles. The mercury atom when it is on this line must have only the normal charge, i.e. it must have regained all but one of the corpuscles it previously lost ; if it had retained two positive charges it would have been on the line corresponding to the atomic weight $200/2$ or 100 ; if it had retained 3, or 4, 5, 6, 7, 8, on the lines corresponding to the atomic weights, $200/3$, $200/4$, $200/5$, $200/6$, $200/7$, $200/8$ respectively. All these except the last have been detected on the plate. The lines corresponding to the multiple charges on krypton, argon, and neon have also been detected. It appears, then, that in a vacuum tube a mercury atom, for example, may be ionized in two ways ; in the one way the atom loses one corpuscle, in the other it loses eight. I would suggest that these two types of ionization may result from the two different types of collision which the atom must experience. The first type is collision with a corpuscle ; since the corpuscle is an exceedingly small body moving with a very great velocity, it can pass freely through the atom, and the collision it makes with the atom is really a collision with a corpuscle inside the atom ; this may result in the corpuscle it strikes acquiring such a great velocity that it is able to escape from the atom ; this type of collision will result in the detachment of a single corpuscle. The second type of collision is when the atom collides with another atom and not with another corpuscle ; the result of this collision may be that the atom suffers a sudden change in its velocity. This change is not at first shared by the corpuscles, so that these just after the collision may have a very considerable velocity relative to the atom. If there are several corpuscles which are comparatively loosely attached to the atom, these may all be detached from it and leave it with a positive charge corresponding to the number shaken out. It is this type of collision which we regard as giving the multiply-charged ions, and we see that the magnitude of the charge is a measure of the number of corpuscles in an atom which are readily detachable from it. We have seen that the greater the atomic weight the greater the charge it can acquire, the maximum charge being roughly proportioned to the square root of the atomic weight, hence the heavy elements have a larger number of detachable corpuscles than the lighter ones.

Another application of the method I should like to bring before

you is the use of it for the discovery and investigation of a new substance. I have in previous lectures said that sometimes there appeared on the plates a line corresponding to a particle with an atomic weight 3 ; this must either be a new element of a polymeric modification of hydrogen, represented by H_3. The other possibility that it is a carbon atom with four charges is put out of court by the fact that it frequently occurs when the carbon line is exceedingly faint, and when there is not a trace of a carbon atom with even two charges, though the doubly-charged carbon atom occurs readily under certain conditions. In addition to this, the carbon atom parabola never approaches the vertical near enough to allow of its having four charges. I thought the study of the substance producing this line would be of interest, and I have for some time been working at it ; and although the research is by no means completed, I have obtained some results which I should like to bring before you.

At first I was greatly hindered by not knowing the conditions under which the line occurred ; although it appeared from time to time on the plates, its appearance was always fortuitous, and sometimes for weeks together the plates would not show a trace of the line. The line sometimes appeared, but why it did so was a mystery, and I could not get it when I wanted it. I began an investigation, which proved long and tedious, to find the conditions under which the line appeared. I tried filling the discharge-vessel with all the gases and vapours described in the books on chemistry without success. At last I tried bombarding various substances with cathode rays. Under this treatment the substances give off considerable quantities of gas the greater part of which is hydrogen, carbonic acid or carbon monoxide. When I came to analyse by the positive rays the gases given off in this way, I found that with a large number of substances these gases contained the substances giving the three lines, so that I was now in a position to get this line whenever I wanted it, and investigate the properties of the gas to which it owes its origin. The question of the gases absorbed and given off by solids is an extremely interesting one, and a considerable number of investigations have been made on it. In all these, as far as I know, the method has been to heat the solid to a high temperature, and then measure and analyse the very considerable amount of gas which is driven off by the heating. As far as I know, no experiments have been made in which the gases were driven off by bombardment with cathode rays. This treatment, however, will cause the emission of gas even when ordinary heating fails to do so.

Belloc, who has recently published * some interesting experiments on this subject, after spending about six months in a fruitless attempt to get a piece of iron in a state in which it would no longer give off gas

* Ann. de Chimie et de Physique [8], xviii. p. 569.

when heated, came to the conclusion that, for practical purposes, a piece of iron must be regarded as an inexhaustible reservoir of gas. There are some interesting features about the emission of gas from a heated solid. If the body is kept for a long time in a vacuum at a high temperature, the emission of gas becomes too small to be detected; if after this treatment the temperature is raised considerably, there will be a further copious emission of gas, which again diminishes as the heating continues. After it has fallen to zero, all that is necessary is to raise the temperature again and you will get a fresh supply of gas ; and as far as my experience goes, after you have got all the gas you can out of the solid by heating it, you have only to expose it to cathode rays to get a fresh outburst. This effect of increased temperature in renewing the stream of gas from the solid seems to me to be too large to be accounted for merely by an increase in the rate of diffusion of the absorbed gas from the interior to the surface ; it seems to be more analogous to the case of the emission of the water of crystallization from some salts. There are some salts, for example, copper sulphate, which when heated lose their water of crystallization in stages ; thus, if the temperature is raised to a certain value, some of the water of crystallization comes off, but the rest remains fixed, and you may keep the salt at this temperature for ever without getting rid of all the water of crystallization ; on raising the temperature, however, fresh water of crystallization is given off.

Something of this kind seems to take place in the case of gases absorbed in metals, and there seem to be indications that there is some kind of chemical combination between the gas and the metal. This absorbed gas may influence the behaviour of the substance. For example, an ordinary carbon filament gives off, when raised to a white heat, large quantities of negatively electrified corpuscles ; but Pring and Parker * have shown that when great precautions are taken to get rid of the absorbed gas, the emission of these corpuscles falls to less than one-millionth of their previous value. It is in the gases given off by certain metals when they are bombarded by cathode rays that I have found an unfailing source of the substance, which I shall denote by X_3, giving the line corresponding to the atomic weight 3. The arrangement I have used for investigating the presence of this gas is shown in Fig. 4. A is a vessel communicating with the bulb B in which the positive rays are produced by two tubes, one of which is a very fine capillary tube, while the other one is five or six millimetres in diameter ; taps are inserted so that one or both of these vessels can be closed, and the vessels A and B isolated from each other. A is provided with a curved cathode such

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* Phil. Mag., xxiii. p. 192.

FIG. 2.

FIG. 3.
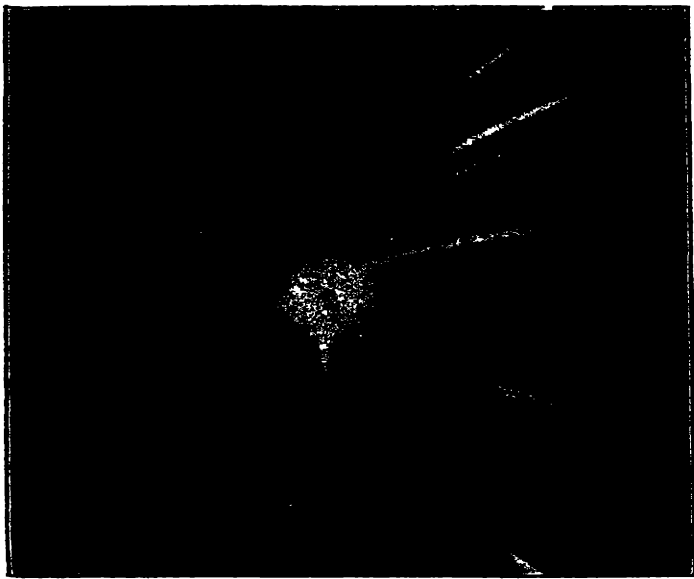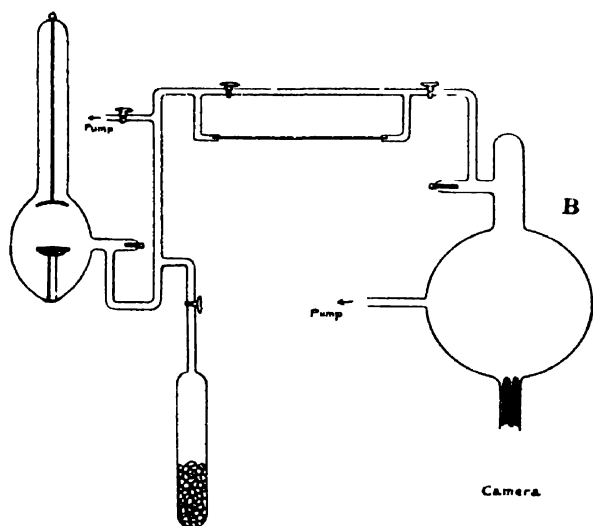
FIG. 4.
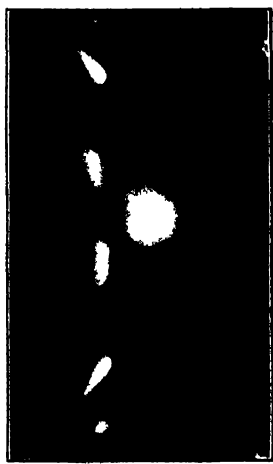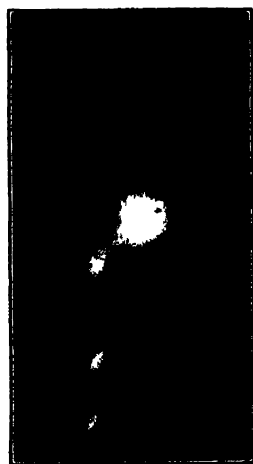
FIG. 5.

as are used for Röntgen ray focus tubes, and the cathode rays focus on the platform on which the substance to be bombarded is placed. [It is not absolutely necessary to focus the cathode rays in this way, but it makes the supply of the gas X_3 more copious.]   After the metal or other solid to be examined has been placed on the platform, the taps between A and B being turned so as to cut off the connexion between them, A is exhausted until the vacuum is low enough to give the cathode rays ; the discharge is then sent through A, and the cathode rays bombard the solid.   The result of this is that in a few seconds so much gas, mainly CO_2 and hydrogen, is driven out of it that the pressure gets too high for the cathode rays to be formed, and unless some precautions to lower the pressure were taken the bombardment would stop.   To avoid this, a tube containing charcoal cooled by liquid air is connected with A, and this absorbs the CO_2 and enough of the hydrogen to keep the vacuum in the cathode ray state.   To see what new gases are given off in consequence of the bombardment, a photograph is taken while the connexion between A and B is cut off.   After this is finished, and when the bombardment has gone on for about four hours, the tap is turned and a little of the gas from A is allowed to go into B ; another photograph is taken, and those lines in the second photograph which are not in the first represent those gases which are liberated by the bombardment, and which have escaped being absorbed by the charcoal.   I have here a slide (Fig. 5) representing the result of bombarding nickel. There are two photographs, one (a) before turning the tap and the other (β) after ; in the second you see the three line very distinctly, while it is absent from the first, showing that the gas giving the three line has been liberated by the bombardment.   I have got similar results to these when, instead of nickel, iron, copper, lead, zinc have been bombarded.   I have tried two specimens of meteorites kindly lent to me from the Mineralogical Museum, Cambridge, and found there the three line.   Nearly every substance I have tried gives, the first time it is bombarded, the helium line as well as this line due to X_3 ; if, however, the same substance is bombarded a second time, the helium line is in general absent (occasionally it is still to be detected, though exceedingly faint) ; and on the third bombardment is invisible in all the substances I have tried except monazite sand, where it is given off in exceedingly large quantities as long as the bombardment continues.   It is remarkable that monazite sand, which contains so many elements, gives no trace of the three line when bombarded.

I have also obtained the X_3 line and also the helium line when the tube A was replaced by one containing a Wehnelt cathode ; with this the current of cathode rays through the tube was much larger than with the other cathode, though the velocity of the rays was smaller.   The Wehnelt cathode gives the line without placing pieces

of metal in the tube, so that in this case nothing is bombarded by the cathode rays but the glass walls of the tube ; the strip of metal forming the cathode is, however, bombarded by the positive rays.

The three line when present at all continues even though the bombardment is very prolonged. In some cases the bombardment has been prolonged for twenty hours, and at the end of that time the line seemed almost as bright as at the beginning ; indeed I could not feel certain that there was any difference. This might lead one to suspect that X_3 was manufactured from the lead or other metal by the bombardment rather than stored up in it, and this view might be regarded as receiving some support from the fact that very little of the X_3 is liberated by heating. The following experiment is an illustration of this. I took a piece of lead, and instead of bombarding it with cathode rays I placed it in a quartz tube connected with vessel A, and heated the tube to a bright red-heat for several hours. Large quantities of CO_2 and hydrogen were driven off by this process ; this was absorbed by charcoal, and the residual gases, which had accumulated in A, were admitted into the vessel B ; the X_3 line and helium line could just be detected, and that was all. I then gave the lead a second heating, this time raising the temperature until the quartz was on the point of softening. The lead was boiling vigorously ; the heating was kept up for about three hours. In this time about three-quarters of the lead had boiled away. I then let the gases which had been given off at the second heating into the vessel B, and took another photograph ; no trace of the line due to X_3 or helium could be detected. The fraction of the lead which had not been boiled away was now placed in A and bombarded by cathode rays. It now gave the three line quite distinctly ; the helium line was visible, but faint. By the bombardment with the cathode rays the lead was only just melted, so that the average temperature was much less than when it was heated in the quartz tube. This rather suggests that the X_3 might be due to a kind of dissociation of the metal by the cathode rays, and not to a liberation of a store of that substance. Another experiment shows, however, that for lead, at any rate, this view is not tenable. I took some lead which had just been deposited from a solution of lead acetate by putting a piece of zinc into the solution, and forming the well-known lead-tree. When I bombarded this freshly precipitated lead, I could get no trace of the X_3 line ; the helium line, too, was absent. I then tried another experiment. I took a piece of lead and divided it into two parts. The first of these I bombarded by the cathode rays : it gave the X_3 line quite distinctly. The other part I dissolved in boiling nitric acid, getting lead nitrate. The nitrate was heated and converted into oxide, and this was bombarded by the cathode rays : it did not give the X_3 line, showing that the X_3 is not produced by the bombardment, but is something stored up in the lead, which can be detached

from it when the lead is dissolved. I have tried several samples of lead ; the one which gave the X_3 line most distinctly was a piece of lead from the roof of Trinity College Chapel, several hundred years old. A sample of Kahlbaum's chemically pure lead, which must, I suppose, at no distant date have been subjected to severe ordeals by fire and water, showed the line quite distinctly, though not so well as the older lead. I have tried similar experiments with iron, and found that iron which gave the three line very distinctly ceased to do so after it had been dissolved in acid.

As the most obvious explanation of X_3 is that it is H_3, bearing the same relation to hydrogen that ozone does to oxygen, and produced in some way from the hydrogen dissolved in the metal, I tried if I could produce it by charging metals with large quantities of hydrogen, and then seeing if the hydrogen coming from the metal gave any traces of H_3. Thus, for example, I tested the hydrogen given off from hot palladium, but found no trace of X_3. I then charged nickel at a temperature of about 355° C. with hydrogen in the way recommended by Sabatier, but found no increase in the brightness of the X_3 over nickel that had not been deliberately exposed to hydrogen. I tried if the brightness of the line would be increased by adding hydrogen to the bulb A, in which the bombardment took place, but found no effect. I also tried adding oxygen to this bulb, thinking that if it was H_3 it would combine with the oxygen, and thus be eliminated, but no great diminution in the intensity was produced by this treatment. The gas seems quite stable, at least it can be kept for several days without suffering any diminution that can be detected ; indeed, when once it has got into a bulb, there is considerable difficulty in getting the bulb free from it. It must be remembered, too, that by the method it is produced the gas is subjected all the time to electric discharges which would break it up unless it possesses very great stability. Thus if X_3 is a polymeric modification of hydrogen, it must possess the following properties :—

1. It must be very stable.
2. It must resist the action of oxygen.
3. It must not be decomposed by long-continued exposure to the electric discharge.

These are properties which a priori we should hardly have expected an allotropic modification of hydrogen to possess.

Mendeleef predicted the existence of an element with an atomic weight 3. According to him this element should be intensely electro-negative and possess the properties of fluorine to an exaggerated extent. The gas X_3 can, however, be kept in glass vessels, which we should not expect to be possible if it possessed more than fluorine's

power of combining with glass. I prefer to defer expressing any opinion as to the actual nature of the gas until I have had the opportunity of making further experiments upon it. It is only about two months ago that I found how to get the gas with any certainty, and, as the method involves long bombardments, each experiment takes a considerable time. This has prevented me from making several experiments which suggest themselves, and which ought to be made before coming to a final decision. I thought, however, that the investigation, though incomplete, might not be unsuitable for a Friday evening discourse, as the gas, whatever its nature, is certainly one of considerable interest, and its detection illustrates the delicacy of this new method.

[J. J. T.]

Active Nitrogen.

EVERYONE has heard of ozone, the active modification of oxygen, which is produced when this gas is subjected to electric discharge. I hope to show you to-night that nitrogen can also be made to assume an active state under suitable experimental conditions. We will begin with an experiment (Fig. 1) which will serve to introduce the subject.

A rapid stream of rarefied nitrogen gas passes through the tube a at a pressure of a few mm. of mercury, and on its way the gas is sparked through by a series of high tension electric discharges from a Leyden jar. It then issues as a jet into the large vessel b,
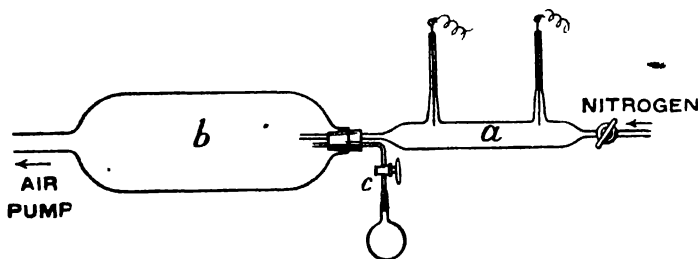
FIG. 1.

where it is seen to be brilliantly luminous, the stream of gas bein visible as a whirling cloud of brilliant yellow light. Notice that this light is of a different colour from that of the electric discharge in the former vessel.

Why does the gas remain luminous in this way for an appreciable time after the electric discharge has passed through it? The view which I shall develop this evening is that the discharge has split the nitrogen molecules into single atoms. Nitrogen atoms in this condition are uneasy, and are anxious to find partners again. But to do this takes time. The reunion of the nitrogen atoms is attended with

the emission of the yellow light which you see, and this continues as long as the process of pairing off is incomplete.

Preliminary to even considering this theory, we must be certain that nothing but nitrogen is necessary to the success of the experiment, and that no other substance intervenes. Some experimenters in Germany have recently expressed the opinion that traces of oxygen are concerned. I am satisfied, however, that they are entirely mistaken. The nitrogen used in the experiment you have just seen has been standing in contact with phosphorus until the phosphorus no longer glows in the dark. If I added a $\frac{1}{1000000}$th part of oxygen to the nitrogen, the phosphorus would begin glowing again quite perceptibly. So we may be sure that there is not that amount of oxygen present; and I do not think it is reasonable to attribute these brilliant effects to a smaller amount. Again, we may enquire what is the effect of adding oxygen intentionally? I find that the addition of 2 per cent of oxygen is enough to obliterate the phenomena altogether. Much more might be said on the subject, but we must pass on.

It is convenient for some purposes to experiment in a different way. We have here two similar glass globes containing rarefied nitrogen. I can induce an electric discharge in them without electrodes by putting them in this coil of wire, through which a Leyden jar is constantly discharging. When I withdraw them you see that they are brilliantly luminous, and that they remain so for several minutes after stimulation. By holding them alternately in the exciting coil we can get them about equally bright, and you see that the luminosity of each decays at about the same rate. Now I stimulate them equally again, and cool one down by immersing it in liquid air. It shines brightly for a moment, but soon becomes quenched. I withdraw it, and you can compare it with the other, which is still brightly luminous.

This experiment shows that cooling the gas shortens the period of luminosity. Let me show you next that the brilliance is increased by cooling. I have exhausted this bulb to a suitable degree, and cool the neck by immersion in liquid air, contained in a transparent vessel (Fig. 2). You see how much brighter the cooled portion is after excitation than the rest of the bulb. There is no doubt a certain ambiguity in this form of experiment, because cooling a portion of the vessel causes a local concentration of the gas in that portion. I must ask you to take it from me that special experiments have proved that this cause is not enough to explain the greatly increased brightness you have seen. The reunion of nitrogen atoms occurs then more quickly the lower the temperature. This is a unique instance of a chemical action being quickened by cooling. In all other cases heating accelerates the action. Plausible objections may be made to this statement, but I must content myself now with saying that they admit of answer.

When oxygen and hydrogen unite, the union may occur in two distinct ways. It may occur with luminosity throughout the volume of the mixture, as when the gases are exploded, or, again, it may occur at the surface of a solid such as clean platinum. In the latter case there is no luminosity.

Similarly, active nitrogen atoms may reunite in the volume of the gas with luminosity—this we have seen already—or the com-

LIQUID
AIR
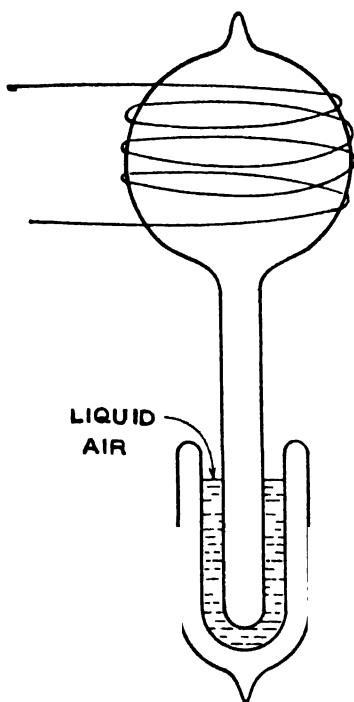
Fig. 2.

bination may occur without luminosity at a suitable surface. Oxidized copper affords such a surface. This bulb (Fig. 3) can be made to glow like those you have seen before, by inserting it into a coil ; and if the copper wire is situated in the side tube the glow lasts a long time, for the gas has as yet no access to it. But if I excite the gas again, and turn the bulb round so as to drop the oxidized wire into it, you see that the luminosity is extinguished in a fraction of a second. Combination of the nitrogen atoms occurs much more quickly at the surface, so that the whole quantity of active nitrogen

present is almost instantly used up.   Incidentally, the experiment illustrates the extremely rapid diffusion of the gaseous residuum in an exhausted vessel, for every particle of the active nitrogen must evidently find its way to the surface of the wire in the fraction of a second.

We pass now to consider the effect of nitrogen in this condition on other substances.   The yellow glow we have studied so far is due to the recombination of nitrogen atoms, and accordingly it shows a nitrogen spectrum, though with very curious modifications.

If we offer to the monatomic nitrogen other substances, it will often unite chemically with them, which of course cold ordinary nitrogen will not do.   I go back to the apparatus used in the first experiment, and admit some acetylene by a stopcock (*c*, Fig. 1). The jet of active nitrogen now enters an atmosphere of acetylene, and you see that the character of the light is at once changed ; it has become lilac.   I turn off the acetylene and substitute chloroform vapour.   We now get an orange light.   This may appear very
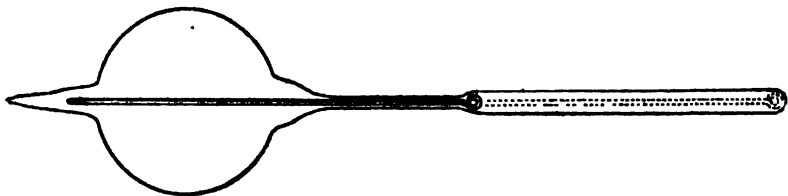
FIG. 3.

different, but the difference is unessential.   The spectrum is in each case that characteristic of cyanogen and its compounds, only the violet portion of this spectrum is more intense with acetylene, the red portion with chloroform.

Since we get the cyanogen spectrum without having any cyanogen compound originally present, we may suspect that some such compound has been formed.   Let us pass from suspicion to proof. Using chloroform vapour from a bulb containing the liquid (*see* Fig. 1), we pass the gases through a vessel in which a test-tube is inserted.   This test-tube contains liquid air, and any condensable constituent is frozen out on to its external surface (Fig. 4).   After a few minutes' run, we take out the test-tube and dip it in a solution of potash.   I now add a mixture of ferrous and ferric salts and excess of hydrochloric acid.   I pour out the liquid on to this white porcelain dish, and you see that abundance of prussian blue has been formed. This proves the presence of some cyanogen compound.

We can get the same result with pentane, ether, benzene, or almost any other organic vapour.   With these the amount of cyanogen formed is much the same, but the cyanogen spectrum, curiously

enough, is far less conspicuous.   Benzene, for instance, almost quenches the nitrogen glow, and little can be seen of the cyanogen spectrum either.   In most cases it appears that hydrocyanic acid is formed, but the orange cyanogen glow, only obtained in compounds containing much chlorine, is probably due to the formation of chloride of cyanogen in addition.   This, when absorbed in potash, forms a cyanate, which has been detected chemically.

In the case just considered, the spectrum observed, when active nitrogen is mixed with another substance, is that of the product of
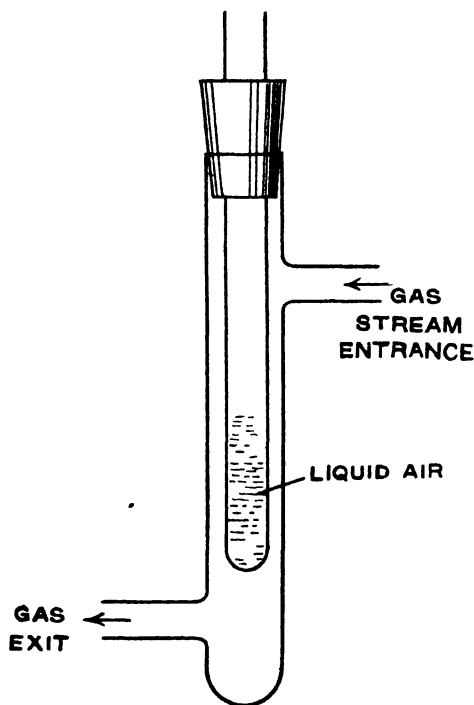
FIG. 4.

the action.   In some cases, however, the spectrum developed is that of the substance originally introduced.   I admit some of the vapour of perchloride of tin : you see the brilliant blue glow.   I introduce a drop of the liquid chloride on a wire loop into the flame of a Bunsen burner, and you see the same blue colour, though less advantageously. The brilliance of the luminous effect does not seem to give any trustworthy indication as to whether much chemical action is going on.   If, for instance, we admit bisulphide of carbon vapour to the

active nitrogen stream, we do not get very brilliant effects of luminosity—nothing striking enough to be worth showing you—but none the less interesting chemical actions are going on. The tube in which the action occurs gets covered with the dark blue transparent deposit, which I show by projection on the screen. This substance is a known compound of nitrogen and sulphur, originally investigated by Mr. Burt in 1910. If the gases are condensed farther on in the tube by liquid air, we get a second deposit of brown colour, which can be identified as the brown polymeric carbon monosulphide studied by Sir James Dewar and the late Dr. H. O. Jones. You see, then, that the chemical action is completely traced. Active nitrogen takes part of the sulphur from carbon disulphide, leaving carbon monosulphide.

The behaviour of active nitrogen with metallic vapours is of interest, though it has not yet been very completely studied. I select the case of mercury to show you. We pass the stream of glowing gas through this tube, which contains a small pool of mercury. While the mercury is cold, the yellow glow passes on unaffected. I apply heat, and green mercury light, of the colour familiar in the mercury vapour lamps used in electric lighting, is apparent, when active nitrogen mingles with mercury vapour. Soon the tube gets obscured, except when I am actually heating it, by a dirty looking solid deposit containing much metallic mercury.

I wish to convince you that an explosive compound of nitrogen and mercury has been formed. For this purpose, to save the trouble of dismounting the tube already used, we will take a similar one prepared beforehand. I heat the mercurial deposit moderately over a Bunsen burner, and, if you will kindly be quite still for a moment, we shall hear a distinct crackling sound, as the explosive compound decomposes. At close quarters it is easy to see flashes of light accompanying the minute explosions, but these can scarcely be shown to an audience, as the opaque deposit over the greater part of the tube obscures them.

It has only been possible this evening to bring forward a selection of the results of two years' work on this subject at the Imperial College, with generous help from colleagues, and facilities provided by the Governors.

Let me conclude by reading to you a prophetic passage from one of Faraday's letters to Schönbein :—" What of nitrogen ? Is not its apparent quiet simplicity of action all a sham ? Not a sham, indeed, but still not the only state in which it can exist. If the compounds which a body can form, show something of the state and powers it may have when isolated, then what should nitrogen be in its separate state ? You see I do not work ; I cannot. But I fancy, and stuff my letters with such fancies (not a fit return) to you."

[R. J. S.]

Friday, March 7, 1913.

The Right Hon. Lord Rayleigh, O.M. D.C.L. LL.D. F.R.S.,
in the Chair.

C. T. R. Wilson, Esq., M.A. F.R.S.

Photography of the Paths of Particles Ejected from Atoms.

[Abstract.]

The phenomena of radioactivity are known to be due to the ejection from the atoms of the radioactive elements of two kinds of particles which travel with enormous velocities : (1) the alpha-particle, which is a positively charged helium atom having a mass four times that of the hydrogen atom ; (2) the beta-particle, which carries a negative charge only half as large as the positive charge of the alpha-particle and has a mass less than the 1700th part of the hydrogen atom.

The velocity of the fastest beta-particles approaches very nearly to that of light, that of the alpha-particles being considerably less but still exceeding 10 000 miles a second.

By the action of Rontgen and other radiations, we can cause electrons or corpuscles which are identical with the beta-particles to be expelled from the atoms of any element with velocities comparable with those with which the alpha-particles are ejected from radium.

The methods which have been used hitherto in the study of the paths of these projectiles and of the effects produced by them in their flight have been somewhat indirect. The actual paths of individual particles have not been observed ; it has been necessary to investigate the combined effects of a large number of particles.

It is true it has been found possible by two different methods to detect effects arising from the action of a single alpha-particle. Thus Rutherford introduced a method in which effects due to the ions set free along the path of a single alpha-particle could be detected by an electrometer ; again in the Crookes spinthariscope each alpha-particle causes a starlike point of light to flash forth momentarily where it strikes the prepared screen. But it has not been found possible by such methods to detect effects arising from a single beta-particle.

It is plain that a great advance would be made if it were possible to induce each alpha- or beta-particle to leave a visible trail behind it along its whole course and to photograph this trail. This is what is accomplished by the method now described.

Each alpha- or beta-particle, in the course of its flight through a gas like air, traverses large numbers of the atoms of the gas. According to modern theories, such as those developed by Sir J. J. Thomson and Rutherford, each atom may be regarded as a sort of miniature solar system in which the planets are represented by negatively charged corpuscles or electrons ; the forces with which we are concerned being of course electrical and not gravitational. When either an alpha- or a beta-particle passes near one of the members of the system, there are forces tending to deviate the flying particle from its otherwise straight course and to cause disturbances in the path of the planetary electron ; these may be violent enough to cause the electron to escape from the system. An electron thus set free will become attached finally to some other atomic system, which thus acquires a negative charge, whilst the atom which has lost an electron has been left with an excess of positive electricity. We thus get positively and negatively charged atoms or ions.

Now a method of making visible the individual ions has long been available. Molecules of water or of other vapours attach themselves more readily to ions than to uncharged atoms or molecules. Thus, in the absence of other nuclei on which vapour can condense more readily, such as those called dust particles by Aitken, it is possible to arrange that every free ion shall act as a nucleus and cause the condensation of water vapour, whilst none condenses elsewhere. Each invisible ion may thus be converted into a visible water drop. The supersaturated condition necessary in order that water vapour may condense on the ions is most conveniently produced by the sudden expansion of moist air

The advance which I have recently succeeded in making in the condensation method of studying ionization is this. The ions are now captured and converted into visible water drops in the positions which they occupied immediately after their liberation by the ionizing agent ; the cloud of drops is then at once photographed. Thus the invisible trail of ions left behind along the course of any ionising particle is converted into a visible line of cloud of which a photograph is secured. In this way a record is obtained of the path of each projectile by making visible the atomic wreckage it has caused in its passage through the air or other gas. In many cases the individual ions produced along the tracks are visible in the photographs.

In order that undistorted pictures showing the result of the passage of the various rays may be obtained, it is essential that the expansion should be effected without stirring up the gas. This condition is secured by using a wide shallow cloud chamber of which the floor can be made to drop suddenly and so produce the desired increase of volume (Fig. 1).*

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* The apparatus is described in the Proceedings of the Royal Society, A., vol. 87 (1912), p. 277.

It is hardly necessary to say that the cloud chamber must be freed from dust particles and all nuclei on which water readily condenses This is easily done by repeated expansions, each too small to cause condensation on the ions, any cloud formed being always allowed to settle before making another expansion.

The cloud chamber must be free from ions other than those produced by the ionizing agent under investigation. Since ions are always being produced even under normal conditions within a closed vessel, it is necessary to maintain an electric field between the top and bottom of the cloud chamber, so that they may be removed as fast as they are produced.
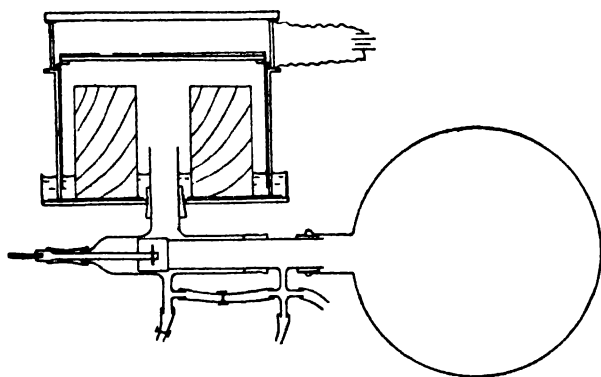
FIG 1

One very practical point in connexion with the cloud chamber remains to be mentioned.   It is necessary that the interior should be maintained in a nearly saturated condition and yet that the roof and walls should be transparent and admit of a clear and undistorted view of the contents.   A glass vessel containing moist air soon becomes coated internally with a dew-like deposit of minute drops. This difficulty is completely avoided by covering the inner surface of the glass with a film of gelatine.

The moist gelatine under the plate-glass roof of the cloud chamber forms a conducting film which is connected through a marginal ring of tinfoil with one terminal of a battery of cells, the other terminal being connected to the floor.   In this way, a nearly uniform vertical electric field is maintained between the roof and floor of the chamber.   The floor is virtually a pool of water made solid by the addition of gelatine and blackened by means of ink so that it forms a dark background for the clouds.   It is supported by a glass plate which forms the top of a hollow cylindrical plunger working in water.

As regards the actual mechanism for causing the sudden drop of the floor of the cloud chamber, it is sufficient to state that the space below the plunger can be put in communication, through wide tubes, with an exhausted chamber by suddenly opening a valve.

In order that the ionizing particle should leave sharply defined cloud trails, it is necessary that they should traverse the moist gas immediately after this has been expanded while the water vapour is still supersaturated to an extent considerably exceeding the minimum which is required to cause condensation on the positive ions (which are more difficult to catch than the negative). Under these conditions, the ions lose their mobility and grow into visible drops before they have had time to diffuse appreciably away from the original track of the ionizing particle.

If the clouds formed by condensation on the ions are to be photographed, it is necessary to expose them to an instantaneous illumination of great intensity while the camera is in position. The instantaneous illumination is obtained by a Leyden jar discharge, the arrangement being essentially the same as that used by Lord Rayleigh in photographing jets of water and by Worthington in his study of the splash of a drop.

I have, however, allowed the spark to traverse mercury vapour at atmospheric pressure instead of air, the brightness being thereby greatly increased.

The spark, of course, has to be suitably timed, so that the cloud trails may be illuminated after the drops composing them have grown sufficiently to scatter plenty of light but before there has been any appreciable disturbance of the air by convection currents.

Figs. 2 to 13 are pictures obtained by this method. It is perhaps necessary to point out they are all photographs of clouds consisting of minute water drops condensed upon ions, for many of them have a very uncloudlike appearance.

Fig. 2 is a photograph of the tracks of some alpha-particles shot out from a minute quantity of radium placed within the cloud chamber, the camera looking down through the plate-glass roof. From the atoms of radium, alpha-particles are continually being projected with velocities of many thousands of miles per second, each producing more than 100,000 ions in the course of its flight. Under ordinary conditions the trail of ions left behind by each particle is invisible ; those formed by particles which have traversed the supersaturated air of the cloud chamber immediately after its expansion, however, are at once converted into visible cloud trails. These form the sharply defined spokes or rays of the picture. The more diffuse cloud rays are the tracks of particles which have traversed the air before its expansion, the ions having thus had time to wander out of the original track before losing their mobility through the condensation of water upon them. The electric field maintained in the

cloud chamber fixes a limit to the age and hence to the diffuseness of the trails which are rendered visible; under the actual conditions any free ions would be driven by the electric force to the roof or floor within less than a fifth of a second after being set free.   None of the ions made visible has had a free existence exceeding this limit.

It is clear that an ionizing particle, while traversing or even passing near to an older trail of ions on which a cloud has already formed, will not find the vapour supersaturated to the extent necessary to cause condensation on the ions; it will therefore fail to leave a visible trail in this region.   This is doubtless the reason why the sharply defined trails only appear to begin at some distance from the source, the older trails being most closely packed in the region around the source

By means of a suitable shutter arrangement attached to the floor of the cloud chamber, it is possible to prevent alpha-particles from traversing the moist air till after the expansion.   The diffuse cloud trails are then absent from the photographs (Fig. 3).

The most remarkable feature of the tracks of the alpha-particles is their general straightness.   Sudden bends are to be observed, however, practically all the rays being bent within a millimetre or two of their ends.   In this respect, as in others, the photographs confirm the conclusions arrived at by less direct methods.

In the next picture (Fig. 4) an enlargement of two of the tracks is shown, one of them having two sudden bends.   The path is otherwise straight except very near its end.   Now the alpha-particle has thousands of encounters with atoms of the gases of the air in each millimetre of its course by which ionization is brought about, as we know from measurements made by the electrical method; and in accordance with this, the cloud particles (which are simply ions magnified by condensation of water) are so closely packed that they are not separately visible in the photograph.   It is remarkable that only two encounters out of the many thousands occurring in the course of its flight should succeed in deviating the particle visibly from its course and that in these cases the deviation should be quite large.

The alpha-particle, in passing near one of the electrons of an atom, may impart to it sufficient energy to cause it to escape from the atom, whilst on account of its own enormous momentum it is not perceptibly deviated from its course.   We can thus understand the general straightness of the tracks.   The sudden deviations must be due to encounters of a special kind; according to Rutherford's view, such large deviations would be caused by the alpha-particle passing near the centre of the atom, where he supposes the positive charge to be concentrated.

What is perhaps the most interesting feature of the particular track I have been describing remains to be mentioned.   At the
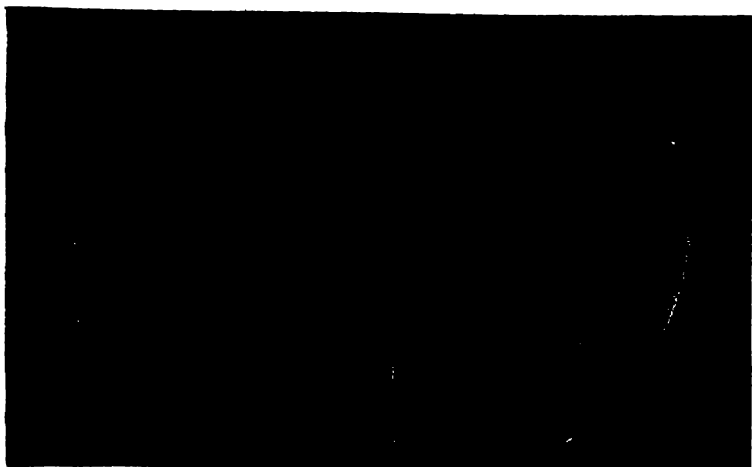
FIG. 2.

FIG. 3.
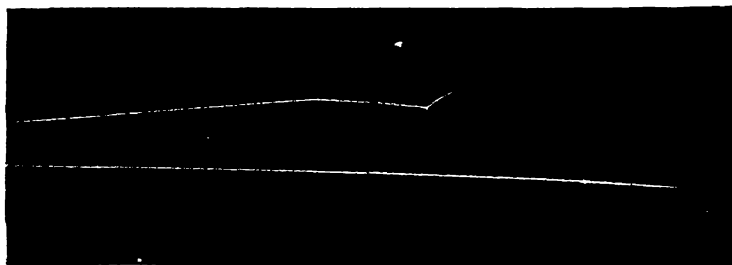
FIG 4.

second of the two bends, there is a distinct spur which one can hardly interpret otherwise than as being due to the recoil of the system which has caused the deviation of the particle.

The next two photographs (Figs. 5, 6) show the effect produced in the cloud chamber by a trace of radium emanation—the radioactive gas which is the first product of the disintegration of radium. Each cloud ray is a visible record of the conversion, by expulsion of an alpha-particle, of a single atom of the emanation into an atom of the next member of the radioactive series. Since the rays start in the gas, it is now possible to get tracks which are complete from beginning to end. The ends are distinguishable by the characteristic bend or hook. At the beginning there is an enlarged head where, moreover, the cloud is of greater density ; this represents ionization by the recoil of the atom from which the alpha-particle has escaped.

It may be noticed there is a sudden bend in one of the rays with which there is again associated a spur-like process.

Radioactive substances emit beta-particles as well as alpha-particles. These produce comparatively few ions along their tracks, which are thus much less conspicuous when converted into visible cloud rays than those of the alpha-particles. They are, in consequence, more difficult to photograph, and they have not appeared in any of the pictures shown thus far.

With suitable illumination, however, the droplets condensed on the individual ions may be photographed, provided they are not too closely packed. It is thus possible to study the path of any ionizing particle, however small the number of ions produced.

On account of the enormous velocities with which they are emitted—closely approaching that of light—the beta-particles are able to travel considerable distances in the air, distances many times greater than the diameter of the cloud chamber. It is therefore impossible to obtain a picture of the whole track of a single beta-particle.

Here, on one plate (Fig. 7) are shown the final portions of the tracks of an alpha- and of a beta-particle. The beta-ray shows much less intense ionization, as indicated by the comparative densities of the clouds ; and its devious path forms a great contrast to the straightness of the alpha-ray.

The beta-particle, of course, is so much more readily diverted from its course on account of its much smaller mass.

If, however, we catch the beta-particle at a sufficiently early stage of its career, we find that its immense velocity compensates for its very small mass and its path may be sensibly straight for distances of several centimetres, in spite of the very large number of atoms which it must traverse. This is illustrated by the next picture (Fig. 8) which shows, in addition to the end of a beta-ray, a portion of the trail left by a beta-particle while its velocity was still very high ; it is

noticeable that it is practically straight. Another result of the high velocity is that very few ions have been set free along this path ; for the faster the particle traverses an atom the shorter is the time during which the forces can act. The individual ions are readily distinguishable in the photograph ; the droplets appear mainly in pairs (each representing a positive and negative ion) but there are, in addition, here and there closely packed groups of twenty or thirty.

In addition to the alpha- and beta-particles, radioactive bodies emit an extremely penetrating type of ionising rays—the gamma-rays —having properties similar to those of Röntgen rays. If we expose the cloud chamber to this radiation (cutting out the alpha- and beta-rays by a lead screen), we see on expansion extremely fine threads of cloud crossing the vessel in all directions. These are the tracks of beta-particles emitted mainly from the walls of the vessel under the influence of the gamma-rays. The whole of the ionization produced by gamma-rays appears to be, as it were, secondary and due to the beta-rays.

The remaining pictures illustrate some of the properties of Röntgen rays.

In studying the nature of the process of the ionization of air by X-rays by means of the expansion apparatus, it is convenient to use an instantaneous flash of the rays produced by sending a single Leyden jar discharge through the Crookes tube. The discharge is so timed that the rays pass through the cloud chamber immediately after the expansion of the air, so that they traverse it while it is supersaturated with water vapour. The ions produced are thus at once fixed by the condensation of water vapour upon them before any appreciable diffusion has occurred ; the illuminating spark is timed to pass a fraction of a second later and so give an instantaneous photograph of the clouds condensed on the ions.

Fig. 9 is a photograph showing the effect of such a flash of X-rays —the radiation being confined to a narrow cylindrical beam by lead screens provided with apertures. The photograph was obtained with the camera pointed horizontally through the cloud chamber in a direction at right angles to the beam of X-rays.

In the light of knowledge furnished by other methods, we may interpret the picture in the following way. Under the influence of the X-rays, an atom here and there in the path of the cylindrical beam of X-rays has emitted a corpuscle or beta-particle with sufficient velocity to enable it to traverse several millimetres or even centimetres of air, ions being set free along its path. It is the paths of these beta-particles or cathode-rays which are made visible in the photograph. The X-rays do not appear to produce any ionization other than that effected through the agency of the beta-rays excited by them, as indeed Prof. Bragg has long maintained.

The only room for difference—apart from their mode of origin—
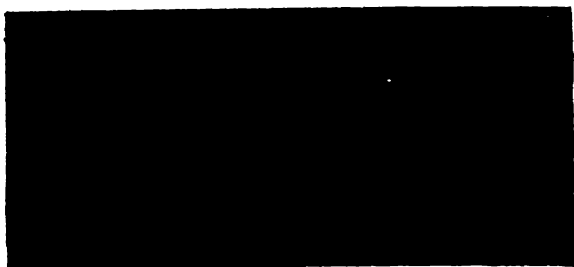
FIG 5.
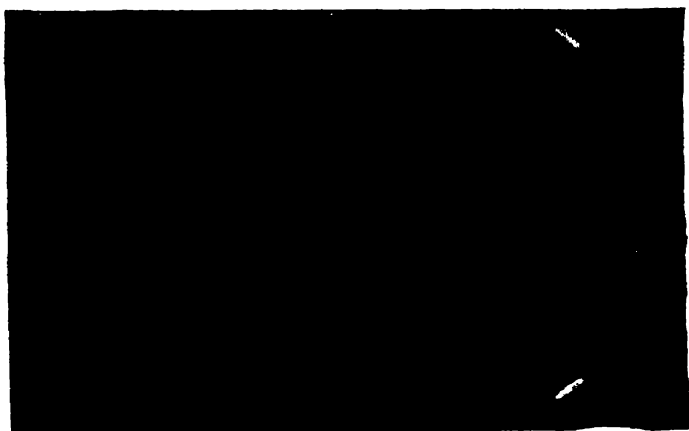
FIG 6
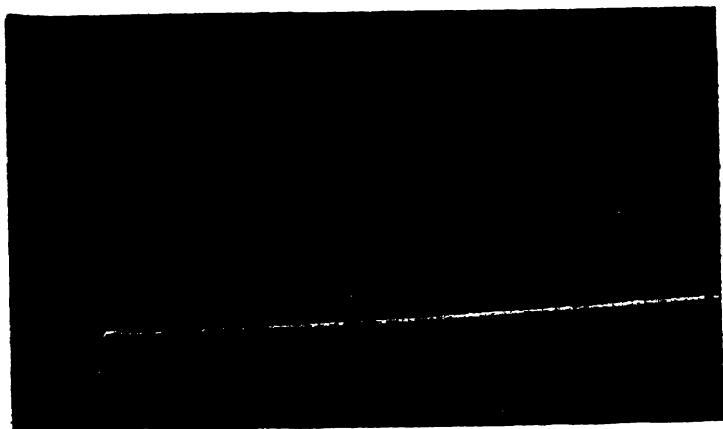
FIG. 7

FIG 8

FIG 9
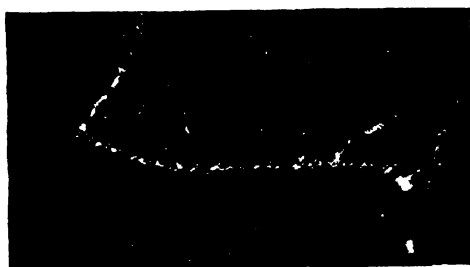
FIG. 10

between the beta-rays produced by the action of X-rays and those emitted spontaneously by the radioactive substances lies in their initial velocity ; for there is no lack of evidence that all negatively charged corpuscles are alike, except in so far as their properties are affected by their velocity. And in fact, the tracks of the beta-particles or cathode-rays excited in air by X-rays are indistinguishable from the end portions of beta-ray tracks, such as are shown in Figs. 7 and 8.

The tracks are far from straight, and as the particle approaches the end of its course the deviation becomes generally more and more marked, the particle being more easily deflected the smaller its velocity.

The departure from straightness is mainly of the nature of a general curvature due to an accumulation of inappreciable deflections at successive encounters ; sudden deviations through large angles, the result of single encounters of a more effective kind, also appear occasionally.

The number of ions produced per centimetre is known to increase rapidly as the velocity of the cathode-ray particle diminishes. This is shown by the increased density of the clouds towards the ends of the tracks.

Fig. 10 is an enlargement of a portion of the track of a beta-particle emitted in air exposed to X-rays. The individual ions are clearly visible and may readily be counted ; the number per centimetre amounts to about 188 pairs, when reduced to atmospheric pressure.

In taking the photograph shown in Fig. 11 the X-rays were made to traverse the air before instead of after the expansion. The ions liberated along the track of each cathode-ray were thus free to move under the action of the vertical electric force maintained in the cloud chamber, the positive travelling downwards, the negative upwards. Each trail was thus divided into two portions, one consisting of negative, the other of positive ions, before being converted into visible cloudlets by expansion of the moist air ; the ions of each trail have also had time to be considerably scattered by diffusion.

The representations of X-ray clouds shown thus far have all been from photographs taken with the camera pointed horizontally and so placed that a magnified image was obtained. The remaining photographs were obtained with the camera pointed vertically downwards, the conditions being such that the whole visible contents of a horizontal stratum of the cloud chamber, about 2 cm. in thickness, were photographed just as in the case of the alpha-ray pictures. Very intense illumination is required to make the cathode-ray tracks visible in a picture taken in this way ; and it is only recently that I have succeeded in photographing them.

A thin sheet of copper was fixed in the centre of the cloud

Fig. 11.

Fig. 12.
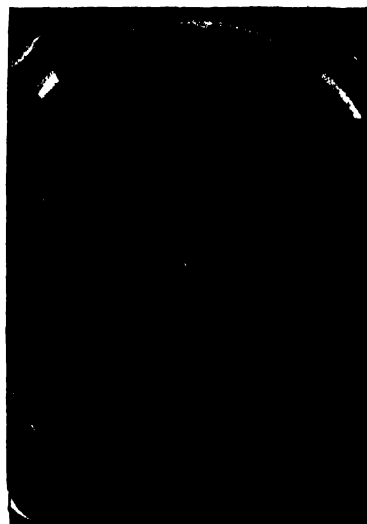
Fig. 13.

chamber in the path of a narrow beam of X-rays, which was made to traverse the supersaturated air of the cloud chamber immediately after its expansion.

The absorption of X-rays by the copper is evident at a glance (Fig. 12) from the difference of the density of the clouds condensed on the incident and transmitted beams.

In passing through the copper the X-rays produce immense numbers of cathode-rays which form dense clouds immediately in front of and behind the copper plate. The clouds are not quite in contact with the copper, the clear space next the plate being due to the air becoming warmed by contact with the copper before the passage of the rays, so that the ions fail to find the supersaturation necessary for their growth into water drops.

From the researches of Barkla and others we know that when exposed to X-rays the copper plate will emit secondary rays—the homogeneous or characteristic or fluorescent rays of copper. These will in turn cause the air to emit secondary cathode or beta-rays The visible cloud trails left by these are seen in the photograph (Fig. 12). A photograph of this kind shows at once the distribution of the secondary radiation from a substance as well as the nature of the cathode-rays produced by this radiation in the surrounding gas. The cathode- or beta-rays produced in air by the copper-rays are all much alike in length (about 1 mm.); this is in striking contrast to the very varying length, ranging up to 2 or 3 cm., of those produced by the primary X-rays.

A photograph taken under similar circumstances with a silver plate in place of the copper one shows similar effects, but the cathode-rays produced in air by the silver rays are many times as long.

Some photographs were also taken with X-rays incident upon the copper plate after their intensity had been reduced by interposing a considerable thickness of aluminium. This cuts out especially the less penetrating radiation. The individual cathode-rays which start from the copper are now readily seen (Fig. 13); they were before too closely interlaced to be separately visible. The surprising feature of this photograph is the great length of some of the cathode-rays emitted by both copper and air exposed to the X-rays. Some of the tracks are about 3 cm. in length when the air is at atmospheric pressure.

[C. T. R. W.]

Great Advance in Crystallography.

CRYSTALLOGRAPHY has made such remarkable progress during the
last few months, and the position at the present moment is so
interesting, that it was considered opportune to review it in a
Discourse from this historic lecture-table. For, firstly, the descrip-
tions of the crystals of all the ten thousand substances which have
ever been subjected to goniometrical measurement have been collected
together and classified within the four volumes of a monumental work
by Professor von Groth, of Munich. Secondly, this immense labour
has been paralleled by the construction, by Professor von Fedorow,
of St. Petersburg, of a tabular record of the main crystal elements
of all these substances, arranged in a simplified form, and with the
assurance, which has entailed untold labour to achieve, that they
relate to a truly comparative orientation; so that this table is the
index to and basis of a new method of "Crystallo-chemical analysis,"
which enables a trained investigator to identify any well-crystallized
substance from the result of a brief goniometrical examination.
And, thirdly, the whole of these invaluable results have been placed
on a firm experimental basis; for the internal structure of crystals,
as imagined in all its wonderful details by the greatest geometrical
and mathematical minds amongst us, has been revealed on the
photographic plate as the result of direct experiment with the
excessively minute and all-penetrating wave-motion, or corpuscular
energy, of the X-rays.

It is easy to prove that a crystal has an organized structure. The
fact is at once revealed by the influence of rapidity or slowness of
growth on its character. For example, if a little benzoic acid be
melted on a glass plate over a spirit lamp and the plate allowed to
cool rapidly in the air, on the object-stage of the projection polari-
scope, using crossed Nicols, the dark field is almost immediately
illuminated by crystals beginning to grow at the margin of the liquid
film, and from each bright spot a crystal-needle darts, with fiery tip,
like a lightning flash, into the centre of the field, until the whole
picture is an interlacing mass of acicular crystals brilliantly coloured

Fig 1 —Crystallization of Ammonium Chloride
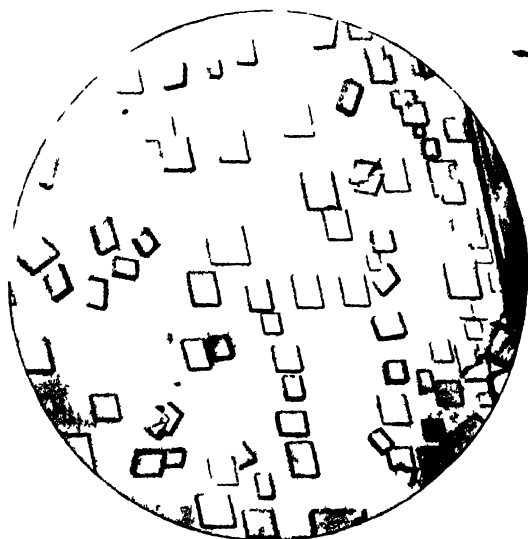
Fig 8 —Parallel Growths of Sodium Nitrate on Calcite

in the polarized light, which renders them more visible. Again, if we crystallize a substance from solution, say potassium bichromate, it entirely depends on whether the degree of supersaturation is slight, the "metastable" condition of Miers and Ostwald, or excessive, the "labile" condition, as to what kind of crystal we obtain. From the metastable solution perfect little single crystals are started into slow growth, by the advent of germ-crystals of the same or an isomorphous substance from the air; while the labile solution spontaneously and rapidly crystallizes in the beautiful feathery forms illustrated on the screen. Ammonium chloride (Fig. 1) and metallic silver afford us even more beautiful screen pictures of arborescent crystallizations, and nothing can exceed the beauty of snow crystals, an example of rapid crystallization of water-vapour. For goniometry these labile forms are useless, but, nevertheless, they teach us much concerning the structure of crystals. For in them the skeleton, or inner framework and plan of architecture of the crystal is revealed.

It is hard to realize the clearly proved fact that our atmosphere teems with excessively minute crystals—for they possess the complete organization of a crystal—often not exceeding the one thousand millionth of a milligramme in weight, and capable, whenever they fall into a quiescent slightly super-saturated solution of a crystalline substance of like structure, of calling forth its power of crystallizing. In order to be able to exercise this remarkable power, however, the germ crystal must be isostructural in a very strict sense, if not identical with the substance which is set crystallizing. Not only must its symmetry be similar, but the dimensions of its structural units—the "bricks" of the crystal edifice, so to speak—must be all but identical. The conditions are, indeed, similar to those required for the facile formation of parallel growths of one crystallized substance on another, so admirably investigated by Barker.

Perhaps the most striking cases for the purpose of illustration are those of the rhombic alkaline sulphates, selenates, perchlorates, chromates, or other of the well crystallized salts of the alkali metals potassium, rubidium, and cæsium, and of the base ammonium which is so extraordinarily capable of replacing them. In any such group of salts the periodic law of Newlands and Mendeléeff is most beautifully illustrated by the regular progression of all the properties of the crystals of the three metallic salts, corresponding to the progression in the atomic weights of the metals, the salt of rubidium, the metal of intermediate atomic weight, having invariably intermediate properties, both morphological and optical. A slide showing the gradual slight change in the prism angle of the crystals of the sulphates will make the point clear, the slope of the prism face of rubidium sulphate being intermediate between the greater slope of that of the potassium salt and the lesser slope of that of the cæsium salt. The variation of the position of the optical ellipsoid in the three monoclinic double sulphates of the $6H_2O$ series containing these three salts is also illustrated by a slide in which the ellipsoid can be rotated through the three

positions (the rotation being also indicated in Fig. 2 by the dotted ellipses) In a similar manner the dimensions of the structural units—the molecular volume (that of the "brick" regarded as a molecule) and its expression in the three dimensions of space (which we now have a means of determining, by combining the density and the crystallographic axial ratios, and which are known as topic axial ratios)— vary in regular progression as functions of the atomic weight. Hence, the structural dimensions of the two extreme members of any of these groups of salts, the potassium and the cæsium salts, are most divergent, and Barker has shown that while the rubidium salt will in general form parallel growths with either the potassium or the cæsium salt, the potassium and cæsium salts themselves will never form satisfactory parallel growths on each other, clearly owing to the disparity in the dimensions of their structural units. Further, the ammonium salt of any group has the interesting property of forming crystals of which the mole-
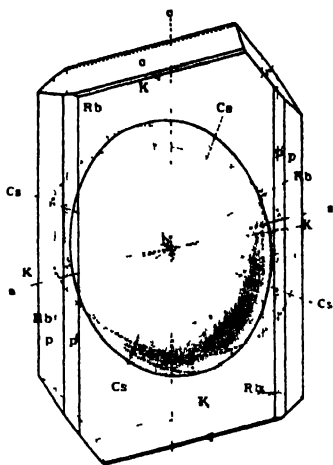
FIG. 2.—ROTATION OF THE OP- TICAL ELLIPSOID OF THI DOUBLE SULPHATFS ON REPLACING POTAS- SIUM BY RUBIDIUM OR CÆSIUM

cular volumes and topic axial dimensions are almost identical with those of the rubidium salt of the same group. Now it is most important and conclusive that the ammonium and rubidium salts form the best of all parallel growths ; they are, indeed, no longer merely parallel growths. but zonal growths and complete overgrowths. They also form excellent mixed crystals, and in every way which has yet been experimentally tested they show the nearest approach to true iso-structure. Some photographs of such parallel growths of rubidium and ammonium salts will render the matter clear. There is also one case of iso-structure investigated by Barker, that of calcite and sodium nitrate, which is of particular interest ; for these are not chemically iso-morphous substances, but they happen to have similar rhombohedral symmetry and almost identical molecular volumes and topic axial dimensions. The slide of parallel growths of sodium nitrate on calcite (reproduced in Fig. 3, Plate I, by the kindness of Mr. Barker) is very striking and conclusive. Barker has recently suggested the nature of the structure of these two substances, two molecules forming the unit " brick," as represented in the slide exhibited. In the case of potassium sulphate and its analogues, one molecule forms the " brick," as represented by the next slide.

It has thus been proved experimentally from the morphological side that a crystal has a definite structure, and that its unit " bricks " or " cells " have definite and measurable dimensions. But the fact is equally well demonstrated optically. We have only to pass a beam of light through a 60° prism of a non-cubic crystal, for instance, quartz, to see at once the radical difference of effect from that given by glass or other non-crystallized substance. For instead of the usual single spectrum produced by glass the quartz prism refracts two distinct spectra, unless it happens to have been cut so that the light traverses the unique direction of single refraction, coincident with the axis of the natural quartz crystallographic prism, which is also the axis of trigonal (threefold) symmetry. The quartz prism used in the experiment is cut at right angles to this direction, so that the axis and refracting edge of the cut prism are parallel to the natural axis, and the separation of the two spectra, corresponding to the two refractive indices of quartz, is thus at a maximum. Moreover, on placing a Nicol prism in the path of the refracted rays, we observe that the light producing the two spectra is oppositely polarized, one spectrum extinguishing when the Nicol has its vibration plane vertical, and the other when the Nicol is rotated so that the vibration plane is brought into the horizontal position. The crystal thus possesses a structure, which is capable of separating a beam of ordinary light into two beams, having definite and perpendicularly different vibration directions.

Again, we see proof of structure if we cut a plate out of the crystal and examine it in a converging beam of polarized light, especially if the crystal, say one of calcite, be cut perpendicularly to the singular axis (or to the bisectrix of the two such axes in the cases of biaxial crystals) of single refraction. A beautiful interference figure is produced, composed of spectrum-coloured rings and a black cross, that is, a figure symmetrical about the axis of trigonal symmetry and of single refraction. This evidence of structure can be most wonderfully reproduced by glass, if we strain the glass by heating and rapid cooling about a cylindrical axis, but an ordinary unstrained piece of glass affords no such effect at all. It is clear, therefore, that the calcite crystal has a symmetrical structure about the axis of single refraction. Similarly, the beautiful biaxial interference figure exhibited on the screen, afforded by a plate of rhombic potassium nitrate, is symmetrical about the centre of the double-looped figure of spectrum-coloured lemniscates.

Sufficient evidence will now have been brought forward that a crystal is endowed with a definitely organized structure. In the crystal of a pure substance we are dealing with a chemical element or compound, and if with the latter it may be of any grade of complexity, from a very simple binary compound to a most highly complicated one composed of a large number of atoms. If the crystal be that of an element the structure is obviously composed of

the similar atoms of that element, while if it be a compound we have a structure composed of atoms of as many kinds as there are chemical elements present combined in the substance, and in the same relative proportion as is expressed by the chemical formula of the substance. In the case of a compound, moreover, the structure may also be considered to be that of the molecules of the substance, for they or a simple arrangement of a small number (group) of them form the grosser units of the structure, whilst the atoms are the ultimate units.

Suppose we now represent this molecular or polymolecular grosser structural unit by a point, and that such point be analogously situated within each unit. The essence of crystal structure then is that these points are so arranged in space that if they are joined by imaginary lines the latter form a " space-lattice " (German, " Raumgitter "), each unit cell of which may be conceived to be the " brick " already alluded to, and the domicile of the chemical molecule or group of molecules (indeed, it is immaterial whether the points are considered as placed at the corners or in the centres of the cells) or, in the case of an elementary substance, of a group of similar atoms. We may, therefore, define a crystal as follows :—

" A crystal of any definite chemical substance consists of a homogeneous arrangement of grosser units of matter, each consisting of one chemical molecule or a small group of molecules of the substance, and the kind of arrangement is such that these grosser units are all identically (sameways, parallelwise) orientated, and that their analogously chosen representative points, one from each such grosser unit, form a space-lattice (Raumgitter)."

There are fourteen kinds of space-lattices, slides of several of which are exhibited on the screen. Three possess full cubic symmetry, two are tetragonal, four are endowed with rhombic symmetry, and two are monoclinic ; while triclinic, trigonal, and hexagonal crystals have each one space-lattice corresponding to their type of symmetry. In every case it is the full (holohedral) symmetry of the system which is present, no space-lattice possessing merely the lower degree of symmetry corresponding to one of the so-called hemihedral or tetartohedral classes of the system in question.

Now in the solid crystal, not only are the grosser units arranged so that their representative points are repeated in space with extraordinary accuracy of position, with production of unit cells or " bricks " of absolutely identical dimensions throughout the crystal, but the shapes of the grosser units themselves are identically similar and identically similarly orientated in space. Suppose, however, that the force of crystallization, the directive molecular force concerned in bringing the molecules together in this regular order of marshalling, is only adequate just to attain this marshalling of the grosser units into a space-lattice formation, without being able to fix the units about their own centres of gravity, a certain amount of wobbling about the latter being still permitted. We might, in such circum-

stances, expect that some of the properties of a crystal, dependent on the space-lattice formation on lines of definite symmetry, such as the optical property of double refraction and polarization of light, would be developed and exhibited, while the production of exterior plane faces would be either only partial, with rounded edges and the exhibition of plasticity and viscosity, or would not be achieved at all, the objects produced being still fluid. One cause of such a condition of partial success at crystallization might well be that the substance was composed of a large number of atoms arranged in a long chain, such as the well known " long chain compounds " of organic chemistry, which would offer considerable resistance to marshalling. The author believes that herein lies the explanation of the remarkable " liquid crystals " which Professor Lehmann has made the subject of his particular study, many of which are of just such long-chain character.

By the kindness of Professor Lehmann, who has sent over specimens of some of the most characteristic of his substances for the special purpose of this lecture, and of Mr. Poser, of Messrs. Zeiss, who construct an admirably convenient form of heating microscope and projection arrangement for demonstrating the formation of liquid crystals and their behaviour in polarized light, it is possible to exhibit some of the typical phenomena of these interesting objects on the screen. The substances in question are chiefly such as form two or more polymorphous forms, each stable within a limited range of temperature, and the liquid crystals are usually the second phase observed on allowing the truly liquid heated substance to cool ; the liquid crystal phase is produced at a definite temperature during the cooling, and persists during a definite interval of temperature during the continued cooling. It either exhibits distinct attempts at the formation of pyramidal or prismatic crystals, more or less rounded at their edges, as in the case of ammonium oleate shown on the screen (Fig. 4), or manifests itself as doubly refractive and brilliantly polarizing drops or streams, such as the drops of para-azoxyanisol, which are set rotating independently by the addition of a little colophonium, as demonstrated in brilliant polarization colours on the screen ; it then suddenly passes with further cooling into the final solid phase, often with the production of brilliantly coloured acicular crystals, as in the case of para-azoxyphenetol exhibited on the screen, or of beautiful star-like or flower-like apparitions, radiating from innumerable centres all over the field, as in the exceedingly beautiful case of cholesteryl acetate. The view here put forth is apparently in agreement with that of Lehmann himself, as most recently expressed both in letters to the lecturer and in a memoir of July 27, 1912, to the Heidelberg Akademie der Wissenschaften, in which he says that in all probability : " Die Rundung der Formen hange zusammen mit der Plastizität der Stoffe und habe ihren Grund in unzureichender molekularer Richtkraft, welche wohl genugt, ein Raumgitter herzustellen, nicht aber regelmassige Treppenstufen, wie
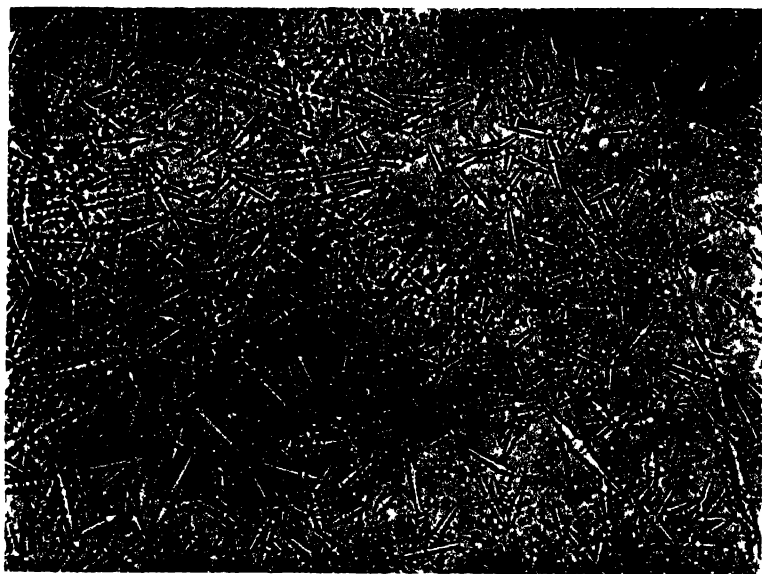
FIG 4—LIQUID CRYSTALS OF AMMONIUM OLEATE
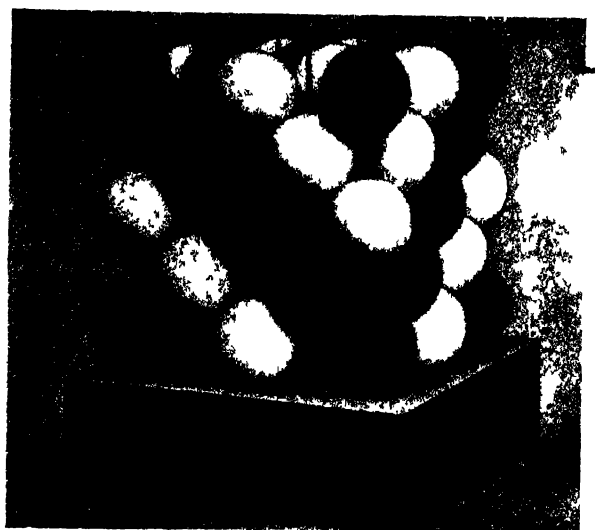
FIG 8—MODEL OF ARRANGEMENT OF ZINC ATOMS (SHADED) AND
SULPHUR ATOMS (LIGHT) IN ZINC BLENDE

es nach Hauys Theorie zur Bildung ebener Krystallflächen nötig wäre." The formation of regular stepped faces (of invisibly minute steps, "Treppenstnfen") the lecturer considers to occur only when the grosser units become fixed about their centres of gravity or representative points, with production of a truly solid crystal.

But now let us pass to the consideration of the internal structure of the grosser or space-lattice units themselves. Their symmetry may be, in simple cases, similar to that of the space-lattice, but in general this will not be so. Whatever the stereometric arrangement of the chemical atoms in the molecule may be, and, if more than one molecule goes to form the space-lattice unit, whatever their mutual arrangement, and therefore, whatever be the outer configuration of the whole unit, when the crystal is a truly solid one, the force of crystallization (now no longer denied) is adequate to fix each space-lattice unit, not only considered as a point with reference to its neighbours, but as regards its shape and its whole character, parallelwise and sameways orientated with respect to its adjacent fellows, and as close as possible to them. Also if more than one molecule goes to each space-lattice unit, their mutual arrangement is achieved on a definite plan, and is the same for every space-lattice unit ; these constituent molecules of the latter are also as closely packed as possible. The final result is thus to produce an assemblage of chemical atoms, in which not only the demarcation frontier between the space-lattice units disappears, but also that between the constituent molecules in the cases of polymolecular grosser units. We come, ultimately, in consequence, to a structure of atoms, each of which we may represent by a point.

Now, just as the genius of Frankenheim and Bravais revealed to us the 14 kinds of space-lattices, so Sohncke made us acquainted with 65 regular systems of points, including many of the 32 classes of symmetry, but not all, which von Lang had shown crystals to be capable of possessing. Later the number was brought up to 230 by simultaneous and wonderfully concordant geometrical researches by Schönflies in Germany, von Fedorow in St. Petersburg, and Barlow in England, and among these 230 all the 32 crystal classes are represented, and no others.

Hence, we come to the conclusion that the skeletal framework of crystal structure is the molecular or polymolecular space-lattice, and the detailed ultimate structure the atomic point-system. The latter determines the class of symmetry (which of the 32 classes is exhibited) and therefore governs any hemihedrism or tetartohedrism, as the development of less than full systematic symmetry used to be called. But it is the space-lattice which governs the crystal system, that is, which determines whether the symmetry is cubic, tetragonal, rhombic, monoclinic, triclinic, trigonal, or hexagonal, and which also determines the crystal angles and the disposition of faces in accordance with the law of rational indices, the law which limits the number of

possible faces to those which cut off small whole-number relat ve lengths from the crystal axes. Indeed, it is because only those planes which contain the points of the space-lattice are possible as crystal faces that the law of rational indices obtains. For any three points of the space-lattice determine a plane in which similar points are analogously regularly repeated, and which is a possible crystal face obeying the law of rational indices. Moreover, those facial planes which are most densely strewn with points are of the greatest crystallographic importance, being what are known as the primary faces, either parallel to the crystal axes or cutting off unit lengths therefrom, as well as being usually the planes of cleavage.

As the space-lattice units are all sameways orientated, any one atom of the molecular or polymolecular grosser unit might be equally well chosen as the representative point of the lattice, so long as a similar choice were made in every space-lattice unit, and the resulting space-lattice would be the same whichever atom were so selected. Consequently, the space-lattice is afforded by the similarly (identically) situated atoms of the same chemical element throughout the crystal structure. The combined point-system (one of the 230 possible point-systems) may thus be considered to be built up of as many identical but interpenetrating space-lattices as there are atoms in the space-lattice grosser unit. These facts are concisely expressed in the definition of crystal structure which was stated as follows by Professor von Groth at the Cambridge meeting of the British Association in 1904.

" A crystal—considered as indefinitely extended—consists of n interpenetrating regular point-systems, each of which is formed from similar atoms ; each of these point-systems is built up from n interpenetrating space-lattices, each of the latter being formed from atoms occupying parallel positions. All the space-lattices of the combined system are geometrically identical or are characterized by the same elementary parallelepipedon."

Having thus arrived at a comprehensive idea of crystal structure on the assumption of each atom and each grosser space-lattice unit being only a point, as far as which we are on safe and assured ground, we may proceed to the consideration of the various ideas advanced concerning the character of the units of structure thus represented by points, that is, concerning the mode in which the space around the point is more or less filled up.

The valency theory of Barlow and Pope considers the atomic point to be expanded into the sphere of the atom's influence, the relative size of which in any one substance is supposed to be proportional to the fundamental valency of the chemical element of' which the atom is composed. The spheres are further assumed to be pressed together on crystallization until they fill space, becoming thereby deformed into polyhedra. The theory of von Fedorow, on the other hand, considers the grosser or space-lattice units to be parallelohedra ; besides those corresponding to the 14 space-lattices there are 9 other

parallelohedra (making 23 in all) composed of simple Sohnckian point-systems compounded of interpenetrating space-lattices. All the 23 parallelohedra are arranged parallelwise, and fill space without interstices. There are, however, only four types, namely, the cube, the rhombic dodecahedron (which has a second vertically elongated variety), the cubo-octahedron, and the hexagonal prism, the first three being all of cubic symmetry, and the fourth of obviously hexagonal symmetry. They are shown, including the second variety of the dodecahedron, in the next screen picture (Fig. 5). He further considers that all four may be homogeneously deformed into analogous parallelohedra of lower orders of symmetry, without ceasing to fill space when closely packed. Hence, von Fedorow concludes that all crystal structures are of either cubic or hexagonal type, including not only truly cubic and hexagonal crystals, but their deformed derivatives. The cubo-octahedron (*e*, Fig. 5) is identical with Lord

a   *b*   *c*   *d*   *e*
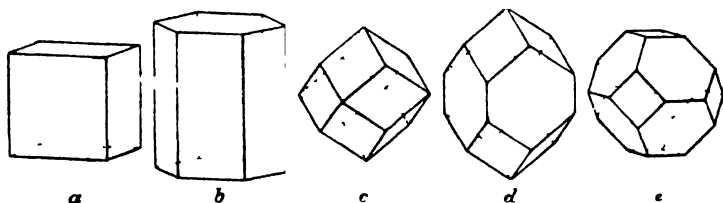
. Fig. 5.—Fedorow's Types of Parallelohedra.

Kelvin's " tetrakaidekahedron," the most general parallel-faced cell (a heptaparallelohedron) into which space can be regularly partitioned, and possessing the minimum surface for a given volume.

Unlike the atomic polyhedra of Pope and Barlow, these parallelohedra of von Fedorow are either molecular or polymolecular, in the latter event being made up of a small number of identically or symmetrically similar sub-polyhedra, termed by him "stereohedra," which represent the chemical molecules, just as already explained, when the grosser space-lattice unit is polymolecular, the stereohedra being arranged to build up the main polyhedron (the space-lattice unit) on a definite plan, which may involve mirror-image juxtaposition. For example, a rhombohedral system of stereohedra is shown on the screen (Fig. 6), consisting of two kinds, R and L, one sort being the mirror-image of the other. Each rhombohedron representing the combined system is composed of six stereohedra, three of each kind, and a series of points, similarly situated one within each stereohedron R, would constitute a Sohncke point-system, while a "double-system" is obtained by adding a series similarly situated one within each stereohedron L. If a single point were taken to represent analogously each rhombohedral set of six stereohedra, we should have a rhombohedral space-lattice produced.

The valency theory of Barlow and Pope may or may not in the sequel prove to be correct, and some facts have recently been brought forward by Barker which tend to show that it will not hold in many cases of inorganic substances. Barker, who has had the good fortune to have worked in St. Petersburg with von Fedorow for more than a year, shows that, as the lecturer has always held, the true unit of volume is the molecular or atomic volume, as determined for the particular substance itself. The molecular volume is determinable by dividing the molecular weight of the substance by the specific gravity of its crystals at a definite comparable temperatue, such as 20 C., but the determination of the atomic volume offers peculiar difficulty, and so far only comparative and indirect methods have been employed, chiefly by Sollas. By taking the volumes of the spherical units to be proportional to the atomic volumes (not those of the
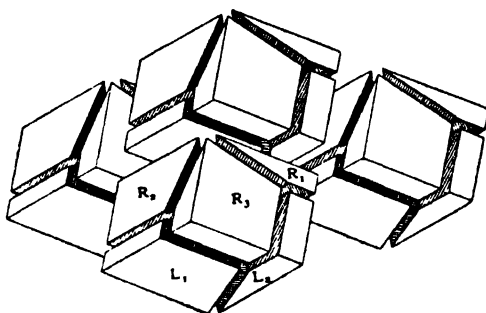
FIG 6.—FEDOROW'S STFRI OHEDRA

element in the free state, as enormous compression occurs on combination), and also determining the amount of free interstitial space by comparative methods of calculation, Sollas has achieved some remarkable explanations of the crystallographic characters of the two polymorphous forms of silver iodide and of the three forms of titanium dioxide, rutile, anatase, and brookite. We have as yet no guidance from von Fedorow as to the nature of the atomic units and the volumes which they occupy. It would not be surprising if the valency volumes of Barlow and Pope, in the cases of those elements for which their theory appears to work in a satisfactory manner, turn out to be identical with the atomic volumes as determined by the method of Sollas. As regards the compounds of carbon and hydrogen, Barlow and Pope have been most successful in accounting for crystallographic and chemical relationships, and it is at least significant that both Le Bas, from experimental work on the molecular volumes of liquid hydrocarbons, and Traube from an entirely different point of view, coincide in assigning the relative volumes 4 and 1 to carbon and hydrogen atoms in combination respectively. If Traube's results

for carbon and hydrogen be accepted, so also must those for the relative volumes of the atoms of the halogens, sulphur, oxygen, and nitrogen, his values being : F = 1 ; Cl, Br, and I = 7 each ; S = 6 ; O = 2 ; and N = 3. As regards oxygen and nitrogen, he agrees with Barlow and Pope, but the latter take all the halogens as of unit valency volume, and sulphur as of valency volume 2. Barker shows that while in the binary sulphides, such as zinc sulphide ZnS, the sulphur is probably of volume 2, in the sulphates, such as K_2SO_4 and $BaSO_4$, it is probably 6, as Traube insists ; this conclusion is also in agreement with other work of Barker on some extraordinary cases of isomorphism, including that of barium sulphate with potassium perchlorate $KClO_4$, potassium permanganate $KMnO_4$, and the extraordinary compound potassium borofluoride KBF_4.

While it would thus appear that the atomic volume (in the substance itself, and including any interspace) is the true effective volume concerned in crystal structure, and that it may be only a coincidence that, in the cases of a few prominent elements, it happens to be approximately proportional to the valencies of those elements (as certainly appears to be true in the cases of hydrogen and carbon, and possibly oxygen and nitrogen), there is a very considerable amount of the joint work of Barlow and Pope which is of permanent value. Their explanations of the preponderating cubic and hexagonal crystalline forms of the elements themselves, and of binary compounds such as ZnS, are doubtless correct, and it will be of great interest, in view of the next development to which attention must be called, to illustrate the case of zinc sulphide, and also the structure of that most interesting simple compound, silicon dioxide SiO_2, quartz, which has been worked out in a very complete manner by Barlow.

Barlow and Pope's idea of the structure of zinc blende, which merely assumes that the volumes of the atoms of zinc and sulphur are approximately equal, is that 16 molecules ZnS go to form the grosser units of the crystal structure, the combined system or space-lattice unit—that is, 16 atoms of zinc and 16 of sulphur. Only one zinc or one sulphur atom in every 16 is sameways orientated, and if we adopt von Groth's definition, we may give the structure of zinc blende as follows : The crystals of zinc blende consist of two interpenetrating regular point-systems, one formed from zinc atoms, and the other from sulphur atoms ; each of these two point-systems is built up from 16 interpenetrating space-lattices, each of the latter being formed from zinc atoms or from sulphur atoms occupying parallel positions. All the 32 space-lattices of the combined system are geometrically identical.

Barlow and Pope have shown that the space-lattice in zinc blende is the third cubic one, in which a point is situated at each cube corner and also in the centre of each cube face. For this is the space-lattice corresponding to an assemblage of spheres of equal volume in closest packing. The space-lattice in question is shown

on the screen (Fig. 7), and a pair of models of the arrangement are illustrated in the next two pictures, in the first of which the points are expanded into spheres of considerable size, and in the second they appear still further expanded into actual contact. The third stage, in which the expansion proceeds until all interstices are filled up and the spheres are converted into polyhedra, is left to the imagination. In the second picture (reproduced in black and white in Fig. 8) the mutual arrangement of the spheres of the two elements in zinc blende, zinc and sulphur, is indicated by the yellow colouring of the sulphur spheres and the grey tinting of those of zinc. The tetrahedral mode of derivation of the structure, accounting for the observed hemihedrism, is also shown in another slide (Fig. 9). The eight larger cubes which together form the grosser unit are each supposed to be occupied by four smaller cubes of the same element, arranged tetrahedrally, and of zinc and of sulphur alternately in different larger cubes; on replacing the little cubes by spheres in contact the model represented in the second picture (Fig. 8, Plate II.) is produced.

FIG. 7.—SPACE-LATTICE OF CENTRED-FACE CUBF.

Barlow's conception of quartz affords us an example in which the symmetry is trigonal, and of which there are two kinds possible, one of which is the mirror-image of the other, the two being helical in character and of the nature of right- and left-handed screws respectively. The two structures, as thus conceived, are represented in the next two slides (Figs. 10 and 11), the white spheres representing silicon atoms and the black ones oxygen atoms, of which there are twice as many, corresponding to the formula SiO_2. The helical character is clearly shown,

FIG. 9.—SCHEME OF TETRAHEDRAL ARRANGEMENT OF ZINC (B) AND SULPHUR (R) ATOMS IN ZINC BLENDE. UNSHADED CUBES UNOCCUPIED.

the white spheres being obviously arranged in a right-handed screw in one picture and a left-handed screw in the other. Right-

and left-handed quartz crystals are so well known that it will not be necessary to do more than illustrate the fact by one or two experiments. First of all, two slides are shown (reproduced together in Fig. 12), one of a right-handed crystal and the
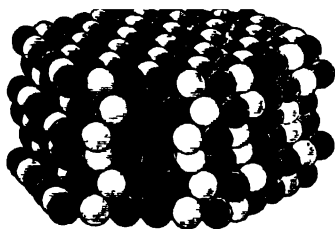
FIG 10 —BARLOW'S CONCEPTION
FOR RIGHT-HANDED QUARTZ
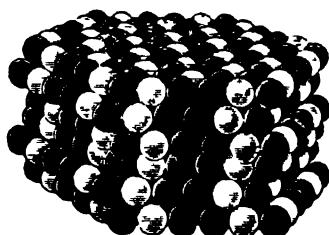
FIG. 11.—BARLOW'S CONCEPTION
FOR LEFT-HANDED QUARTZ.

other of a left-handed one, each exhibiting the characteristic little faces s and x of the right and left trigonal bi-pyramids and right and left trigonal trapezohedra, modifying the right and left corners formed by the meeting of the faces of the rhombo
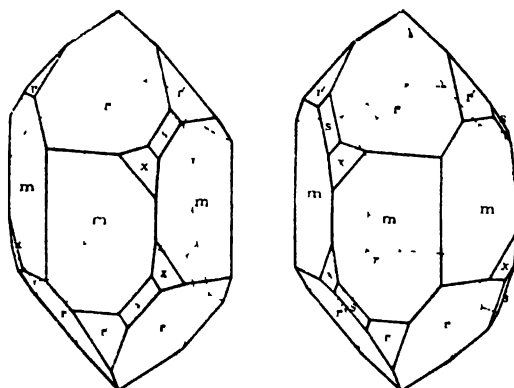
FIG. 12.—THE TWO VARIETIES OF QUARTZ CRYSTALS,
LEFT-HANDED AND RIGHT-HANDED

hedron r and hexagonal prism m. That the right-handed crystal shows rotation of the plane of polarization of light to the right, and the left-handed crystal optical rotation to the left, may be beautifully demonstrated by cutting a plate 1 mm. thick out of each crystal perpendicularly to the axis, and using the device of 24 mica

sectors, due to S. P. Thompson, which between crossed Nicols shows a black cross, the arms of which are deviated one sector to the right or left when the thin quartz plate is interposed, in accordance with the right- or left-handed nature of the plate. Also the phenomenon of the bi-quartz, and of the natural biquartzes often produced by twinning of right and left individuals, may be illustrated, terminating with some beautiful cases of repeated twinning, including amethyst. The imitation of the phenomena of the two varieties of quartz, by crossing strips of mica in a right-handed or a left-handed pile, as shown by Reusch, may also be referred to and demonstrated, as affording some
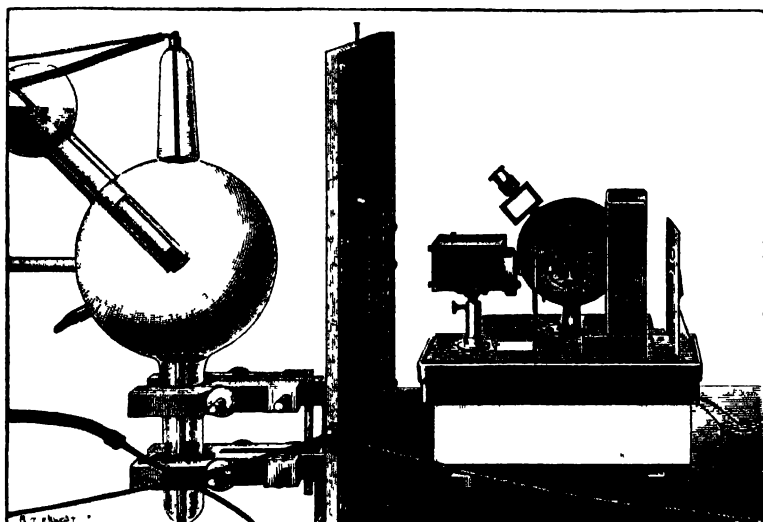
FIG. 13.—APPARATUS OF FRIEDRICH, KNIPPING AND LAUE FOR PASSING X-RAYS THROUGH CRYSTALS AND PHOTOGRAPHING THE EFFECT.

definite proof that the mineral does possess an analogous helical structure, complementarily opposite in its two varieties.

Now these two crystalline minerals, zinc blende and quartz, have been chosen advisedly as examples of crystal structure. For a remarkable series of experiments have recently been carried out by Laue, Friedrich and Knipping at Munich, where the lecturer had the advantage of seeing some of the first photographic results last summer. In these experiments X-rays were passed through crystals of various substances, notably zinc blende, and, in more recent experiments by Laue at Zurich, quartz. The issuing rays were received on a photographic plate, on which they recorded a pattern of spots having the symmetry (full holohedral) of the space-lattice

present as the foundation of the crystal structure. These interesting photographs thus afford the first experimental and visible proof of the truth of the structure assigned to crystals by geometricians and crystallographers. By the great kindness of Professor Laue it is possible to exhibit the original photographs obtained with zinc blende, and one just obtained with quartz, the results for which Professor Laue has not yet published. Dr. Friedrich has also most kindly sent four excellent lantern slides expressly for this lecture.

In view of this further evidence of the richness of the original discovery by Sir William Crookes of the famous tube which is universally known by his name—producing under suitable circumstances of exhaustion the cathode rays when excited by the intermittent
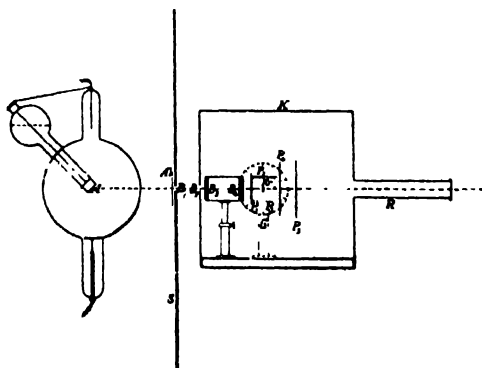
FIG. 14.—DIAGRAMMATIC REPRESENTATION OF APPARATUS OF FRIEDRICH, KNIPPING AND LAUE.

A, Anticathode of X-ray bulb ; B₁, B₂, B₃, B₄, Diaphragms of Lead ; K, Leaden box screen with tubular termination R ; S, Large leaden screen ; G, Goniometer ; P₁, P₂, P₃, P₄, P₅, Photographic plates ; Kr, Crystal ; Al, Aluminium plate

current from a Ruhmkorff coil, which rays, on their striking solid matter such as the soda glass walls of the tube, in turn give rise to the X-rays of Röntgen—it is fitting that some examples of Crookes tubes should be exhibited in action, and Sir William Crookes has been so very kind as to arrange a display of some of his most beautiful productions, including tubes showing cathode rays impinging on a diamond and a ruby respectively, with glowing phosphorescence under the bombardment of the electronic corpuscles, in brilliant colours in each case. By the kindness of Messrs Newton, it is also possible to exhibit in action two recent X-ray bulbs of the particular kind used by Laue and his colleagues.

Two pictures of the actual apparatus employed (one of which is reproduced in Fig. 13), most kindly also sent for the purpose of this lecture, and an explanatory diagram of it (Fig. 14), will enable the

FIG. 15.—SPOT PHOTOGRAPH AFFORDED BY
ZINC BLENDE.

INCIDENT X-RAYS PERPENDICULAR TO A CUBE-FACE, AND
PARALLEL TO A TETRAGONAL AXIS OF SYMMETRY.
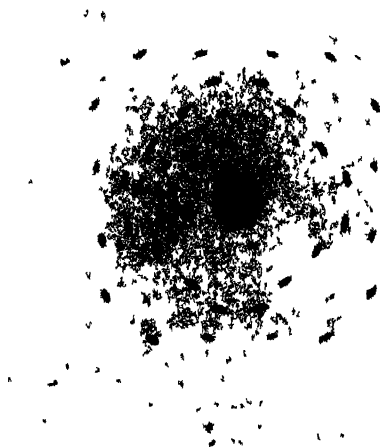
FIG. 16.—SPOT PHOTOGRAPH AFFORDED BY ZINC BLENDE

INCIDENT X-RAYS ALSO PERPENDICULAR TO A CUBE-FACE, AND PARALLEL
TO A TETRAGONAL AXIS OF SYMMETRY, BUT PHOTOGRAPHIC
PLATE TWICE AS FAR FROM CRYSTAL

precise nature of the experiment to be grasped. A plate, 1 cm. square and 0·5 mm. thick, was cut from a good crystal of zinc blende parallel to a cube face, and adjusted on the crystal holder of a goniometer in the path of a very narrow pencil of X-rays from the bulb, isolated by their passage through a succession of lead screens (lead being impervious to X-rays) pierced by small holes. The last screen, which gave the final form to the pencil of rays, was a plate of lead 1 cm. thick, pierced by a cylindrical hole 0·75 mm. in diameter, and fitted with a delicate means of adjustment so that the axis of the boring could be brought exactly perpendicular to the crystal plate. The beam of pure X-rays of circular section, after passing normally through the crystal plate, was received on a Schleussner-Rontgen photographic plate, which was afterwards developed with rodinal.

The developed plate showed an intense circular spot at the centre, caused by the direct X-rays, and a considerable number of other spots of elliptical shape, arranged in a geometrical pattern. Three of these original photographs are exhibited on the screen (and are also reproduced in Figs. 15, 16 and 17). If a series of such photographic plates be used, at different distances from the crystal (as in Figs. 15 and 16), the fact is revealed that the spots are formed by rectilinear pencils of rays spreading in all directions from the crystal, and some of them inclined over 45° to the direction of the incident rays. These deflected beams show similar properties to the original X-rays, ionizing air and helium just like the latter, and with the same degree of variation with the pressure. Hence, there can be no doubt that the character of these deflected rays issuing from the crystal is that of unaltered X-rays, and that they are due to the reflection of X-rays by planes situated at different angular positions in the interior of the crystal. In short, we are in face of reflection of X-rays from planes of atoms in the crystal.

Now a study of the spots reveals the further interesting fact that the pattern shows the full symmetry (that of class 32) of the cubic system to which the crystal belongs, although zinc blende exhibits the slightly lower symmetry of the hexakis-tetrahedral class (31), one of the formerly so-called hemihedral classes of the cubic system. This clearly proves that it is the planes of similar and similarly situated (sameways orientated) atoms in the crystal that are producing the reflections, in other words, the planes of the space-lattice.

At first Laue, who published a separate memoir on the theory of the experiments, considered that it was the space-lattice due to similarly situated zinc atoms which afforded the spot-pattern, as he had been engaged with Prof. Summerfeld in experiments relating to the action of zinc on X-rays. But there appears no reason why the sulphur atoms should not be similarly capable of producing reflections of these extremely fine vibrations or corpuscles, and as the space-lattice is the same for both elements, according to all versions of the geometrical theory of crystal structure, there is really no reason why

PLATE IV
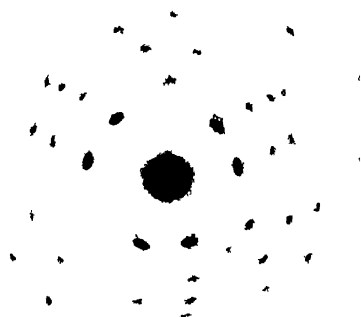
FIG 17 —SPOT PHOTOGRAPH AFFORDED BY ZINC BLENDE
INCIDENT X RAYS PERPENDICULAR TO AN OCTAHEDRON FACE
AND PARALLEL TO A TRIGONAL AXIS OF SYMMETRY
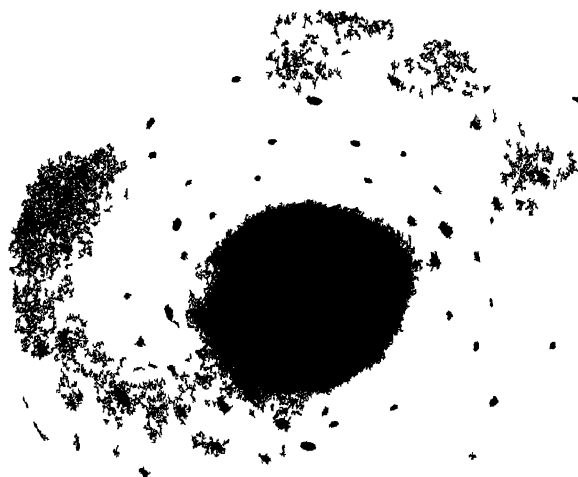
FIG 20 —SPOT PHOTOGRAPH AFFORDED BY QUARTZ
INCIDENT X RAYS PARALLEL TO THE TRIGONAL AXIS

we should not consider the reflections as due to the general space-lattice of zinc blende. Laue considered the "molecules" of the crystal to form a three-dimensional grating—that is, a Raumgitter—and that each molecule is capable of emitting secondary vibrations when struck by incident electromagnetic waves from the X-ray bulb ; also that the molecules are arranged according to the simple cube space-lattice (No. 1). The incident waves being propagated parallel to one of the cube axes (edges), the wave-surfaces will be parallel to the plane of the other two cube edges. He then considers the spots to be interference maxima of the waves scattered by the orderly arrangement of the molecules in the crystal. The equations of condition were next found for interference maxima of direction cosines a, β, γ, and for incident wave-length λ, and from the position of each spot the direction cosine of the pencil of rays which formed it was calculated, assuming all the transmitted pencils to come from the centre of the crystal. Thirteen spots in each quadrant were investigated, and in every case Laue's equations were satisfied ; hence the conclusion that the spots are due to interference of secondary Röntgen radiation appears to agree with the positions of the spots, provided only radiations of certain definite wave-lengths are present in the incident rays.

The lecturer pointed out, in an article in 'Nature,' of November 14th, 1912, that the structure of zinc blende was probably not so simple as had been assumed by Laue, and that the space-lattice with a point at the centre of each side of the cube (No. 3) was the more probable one, the structure being that assigned to it by Barlow and Pope, as already described in this lecture.

A satisfactory explanation has since been advanced by W. L. Bragg, which does accord with this structure and with other essential conditions referred to by the lecturer, which altogether avoids the assumption of only a few wave-lengths, and which agrees with a simple reflection of unchanged X-rays from the planes of points of the general space-lattice of zinc blende. He regards the incident radiation as composed of a series of independent pulses, which, falling on a number of atoms definitely scattered in a plane, are separately reflected, each atom acting as a centre of a secondary wave, and the whole building up a wave-front. The interference maximum is thus due to the reflection of the incident pulses from a system of parallel planes of similar atoms, that is, from one of the parallel series of planes of the space-lattice. Now besides the principal planes of the space-lattice, the cube planes, the points of the space-lattice also lie in a considerable number of other planes, all of which are possible crystal faces corresponding to rational indices. For instance, the octahedral planes are very easily traced, as also those of the rhombic dodecahedron. A minute fraction of the energy of a pulse traversing the crystal will be reflected from each parallel plane in succession, and the corresponding interference maximum will be

produced by a train of reflected pulses. The crystal thus actually manufactures rays of definite wave-lengths, just as a diffraction grating does, the only difference being here in the extremely short length of the waves, which is the very reason why X-rays can penetrate in this manner into the Raumgitter structure. Each incident pulse produces a train of pulses, resolvable into a series of wave-lengths, λ, λ'_2, λ'_3, $\lambda/_4$, etc., where $\lambda = 2\,d \cos\theta$, d being the shortest distance between successive identical parallel planes in the crystal, and θ the angle of incidence of the primary X-rays on the plane of points of the space-lattice. The intensity of any spot depends on the energy in the spectrum of the incident radiation characteristic of the corresponding wave-length, and this varies considerably so that certain parts of the spectrum are much more pronounced than others. Also it depends on the number of reflecting atoms in the plane, that is, on the reticular density of the possible crystal face corresponding to the plane. Hence, the greater the reticular density, the more intense the spot produced in the photograph. As reticular density is also proportional to importance of face, the primary faces having the greatest reticular density, it follows that the most important facial planes reflect the intensest spots, a fact which may prove of great value in enabling us to discover the real primary planes in doubtful cases. Each spot reflected by a plane (considered as passing through the origin and two other points) lies at the intersection of two ellipses, and the figure on the screen (reproduced in Fig. 18), showing an analysis of one of the spot photographs, exhibits this clearly. Indeed, the plane of atoms corresponding to any spot can be found from the two ellipses; for each ellipse is the section of a cone by the plane of the photo-

FIG. 18.—ANALYSIS OF SPOT-PHOTOGRAPH
(FIG. 16) OF ZINC BLENDE.

graphic plate, the axis of the cone being the line joining the origin (centre of the triaxial system, and considered as one of the three points determining the plane) and the particular atom (the second or third point of the three, of definite co-ordinates), and the generator of the cone being the incident beam.

The interesting results of Bragg are in full accord with the assumption of the centred-face cubic space-lattice (No. 3), but not with either the simple-cube or the centred cube space-lattice (Nos. 1 and 2). They also account for the elliptical shape of the spots. The amount of ellipticity depends on the distance of the photographic plate from the crystal. When the two are very close the spots are round, but they become more and more elliptical as the plate is receded (compare Figs. 15 and 16). The phenomenon is due to the fact that the initial rays are not strictly parallel, and the effect will be clear from the next slide (Fig. 19). The vertically diverging rays striking the reflecting planes of the upper part of the crystal meet them at a less angle of incidence than those of the lower part, and so the reflected rays converge. Horizontally diverging rays, however, diverge still more on reflection. Hence the section of the reflected beam is an ellipse with major axis horizontal.

It is of importance to note that the centred-face cubic space-lattice is characteristic both of the arrangement of identically (sameways) orientated and environed atoms of the same element, zinc or sulphur, and of the atoms of both elements regarded as equal spheres in contact. In the slide already shown (Fig. 8, Plate II), of Barlow and Pope's model, the spheres of sulphur are coloured yellow to distinguish them from the grey-coloured spheres of zinc. If we ignore the colour, and consider them as similar spheres, we see that they form the centred-face cubic arrangement. The hemihedral nature of zinc blende is, however, very likely connected with some real difference of volume between the atomic spheres. As the spot figure is holohedral it would appear to be due to the space-lattices of similarly placed atoms of either (but in each lattice only one) element, rather than to the spheres of the combined system of atoms.
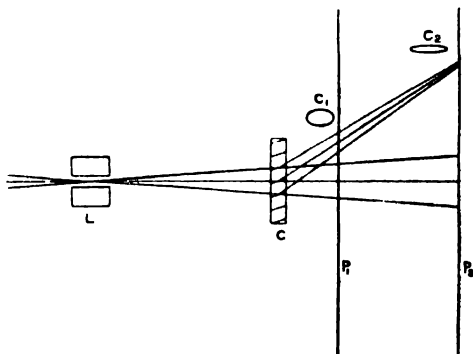
FIG. 19.—EXPLANATION OF ELLIPTICAL SHAPE OF SPOTS.

This latter conclusion is further borne out by the result of the new work by Laue on quartz. The photograph now shown (Fig. 20, Plate IV), so kindly sent by Professor Laue, exhibits the trigonal nature of the symmetry very clearly, and Professor Laue informs me that the same figure is afforded by both right and left quartz, so that it does not reveal the hemihedral character of quartz which has been demonstrated this evening, but possesses the full holohedral symmetry of

the trigonal space-lattice, and exhibits the threefold nature of the axis of symmetry which is perpendicular to the plate and along which the X-rays were directed.

Professor Laue has also experimented with the crystals of a number of other cubic substances, and, like zinc blende, they all show holohedral symmetry about a tetragonal axis.

W. L. Bragg has found that stronger photographs of the same nature can be obtained from mica, using nearly grazing incidence, and it is by use of this fact that Mosely and Darwin have been able to study the reflected rays electrically, and found them to resemble ordinary X-rays.   By the kindness of Mr. Bragg, a diagram of his apparatus and a positive lantern slide of one of his mica spot photographs are exhibited on the screen.   The large white spot is due to the direct rays ; the next brightest but smaller spot considerably above the direct one is due to rays reflected from the cleavage plane, and the other spots to reflections from other possible faces and planes of the monoclinic space-lattice ; all the spots are such as are compatible with this lattice, and with the well known fact that the monoclinic angle is almost 90°.   The spots lie on two ellipses intersecting at the central direct spot and at the upper bright one, each ellipse corresponding to a set of parallel rows of points, the crossing of the two sets forming rhombic parallelograms, the basal edges of the monoclinic prismatic space-lattice cell of mica.

Incidentally these experiments appear likely to throw light on the much-debated question of the nature of the X-rays.   As all the experiments unite in indicating that a fraction of the X-rays suffers reflection at the planes of atoms parallel to the more important possible crystal faces, all being planes of atomic points of the space-lattice, it would appear that the X-rays are some type of wave-motion, or at any rate some kind of pulse with an extended wave-front.   Yet after reflection they retain the same corpuscular character which Prof. W. H. Bragg has shown they possess.   For the liberation of a high-speed electron from an atom traversed by the X-ray cannot be explained, according to Rutherford, unless it be supposed that the energy of the X-ray is concentrated over a minute volume, and can be given up in an encounter with a single atom.   Hence these experiments show that the X-rays possess at the same time the apparently opposite properties of extension over a wave-front and concentration in a corpuscular point.

It appears to the lecturer that the simpler explanation is that we are truly dealing with waves, but that the wave-lengths of the X-rays are excessively short, approaching atomic dimensions.   This view that the X-rays are waves is further supported by the results of some experiments just completed by Barkla, in which a diverging pencil of X-rays was directed on a crystal of rock salt, and the issuing rays received on a photographic plate in the same manner as in the experiments already described.   The developed plate shows a new

phenomenon, namely, striation of the spots obtained by reflection from the planes of atoms of the space-lattice, especially in the reflections from the cubic cleavage planes. The striations are, in fact, true interference bands, due to interference of the reflections from equally spaced parallel planes of the space-lattice. By the kind courtesy of Prof. Barkla, two of these interesting photographs are projected on the screen. On the assumption that the X-rays are waves, and that the reflecting plane is one passing through corresponding portions of single NaCl molecules—which agrees with the choice of a representative point from each simple molecular grosser unit, or of a similarly situated atom of one of the two chemical elements present in each molecule NaCl to act as such representative point of the space-lattice—Barkla has calculated that the wavelength is the one hundred and sixty millionth of a millimetre, $0 \cdot 6 \times 10^{-8}$ mm. If the grosser unit be polymolecular, the wavelength works out larger, being proportional to the cube root of the number of atoms in the molecule. If 8 molecules form the grosser unit of sodium chloride crystals, as suggested by some chemists, the wave-length is found by Barkla to be twice this value, namely, $1 \cdot 2 \times 10^{-8}$ mm.; and if 16 molecules of NaCl are comprised in the grosser unit, as would be the case if Barlow and Pope's structure for the cubic binary compounds be correct (the space-lattice in the case of rock salt being that of the simple cube, No. 1), the wave-length would be still longer, about the seventy millionth of a millimetre, $1 \cdot 5 \times 10^{-8}$ mm. Now it is very interesting that these values are of the same order as those derived from determinations of the velocity of electron ejection, which varied from 1 to 2×10^{-8} mm.

The most trustworthy recent estimations of the size of a molecule of rock salt indicate a diameter about 3×10^{-7} mm. Hence the diameter of a crystallographic molecule 8NaCl would be 6×10^{-7} mm., and of 16NaCl about $7 \cdot 5 \times 10^{-7}$ mm.

It should be emphasized, in concluding the account of this fascinating new field of research, that all these reflections occur in the body of the crystal, and are not surface effects. Cleavage planes usually afford stronger results merely because they are generally primary planes of high reticular density. The effect is sometimes heightened by conducting the X-rays at nearly grazing incidence; but this is by no means necessary, and in Laue's experiments several of the planes were inclined as much as 30° to the incident rays.*

The experimental proof of the existence of the space-lattice imparts all the more confidence in approaching the other great advance which has lately been achieved. The completion of the catalogue of crystallographically measured substances by Prof. von Groth, provokes the question : What more is needed in order to enable a crystallized substance described in the book to be recognized by means of a few measurements on the goniometer ? For it is now

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* See Appendix, last page.

proved up to the hilt that, except in the cases of cubic crystals identical in angles in accordance with their perfect symmetry, every solid crystallizable substance is characterized by its own peculiar crystalline form and interfacial angles. This is quite true, even to the last minute of angular measurement, when the conditions of crystallization are ideal. When thus perfect, even iso-morphous substances show differences among themselves to the extent of a definitely measurable number of minutes. But such perfection of growth is not easy to attain, and, in ordinary crystallization with-out special precaution against disturbance, is rarely found. The essential crystallographic measurements can, however, be made in an hour's time, provided use be made of the two- or three-circle form of goniometer, such as the excellent one devised by Dr. Herbert Smith. This form of goniometer enables all the needful measurements of the interfacial angles to be made with a single setting of the crystal on the wax of the holder. But practical difficulties have hitherto still stood in the way. Excellent as is von Groth's classification—and the most suitable for a work of reference of the full and comprehensive character of this per-manent monument of the master's industry and wide knowledge of chemistry, related compounds being arranged and compared in close proximity—the very nature and size of such a work renders it unsuitable for the purpose of discovering rapidly the chemical com-position of a substance from its geometrical elements. An index of substances arranged in the order of their symmetry and the numerical values of the crystal constants within the system is what is needed, and this has now for the first time been drawn up for the ten thousand measured substances by Professor von Fedorow.

Another difficulty then presents itself. It often entirely depends on how a crystal is held in space, that is, which direction in it is to be the vertical axis, which the right-and-left axis, and which the front-and-back axis, as to what the nature of the crystal constants (elements) will be. Moreover, even if two different observers choose these similarly, they may select a different parametral plane (a fourth face other than the three faces parallel to the axes, and cutting off unit lengths from the latter) to determine the axial ratios. Hitherto, beyond a few arbitrary rules—for instance, that the right-and-left axis of a rhombic crystal shall be longer than the front-to-back one—there has been no definite guiding principle for the determination of the setting. Professor von Fedorow has now given us one, by means of which we can be sure which are the real vertical faces (prismatic or pinakoidal), which is the basal plane (the pair of top and bottom faces), and which set of pyramid faces are the important ones fixing the relative axial lengths. The true setting has been determined by Professor von Fedorow for every one of the substances in his index, and the crystal elements for such setting calculated.

The mode of classification adopted in this index-catalogue is based

on the values of the five fundamental angles which, in general, characterize the crystals of any specific substance. A cubic crystal has definite angles which are entirely fixed and rendered invariable by reason of the perfect symmetry. At the other extreme come triclinic crystals, the general case, in which all five fundamental angles are different and quite independent of each other. On monoclinic crystals there are three independent angles, from which the other two can be calculated. Rhombic crystals have only two independent angles, which, if measured, enable the other three to be calculated. Hexagonal, tetragonal, and trigonal crystals possess only one angle independent of the symmetry, determinative of the relative length of the unique axis of hexagonal, tetragonal, or trigonal symmetry.

The first object of von Fedorow in order to arrive at the correct setting, is to decide which are the primary axial-plane and parametral faces; and he is wonderfully aided here by the discovery of the fact
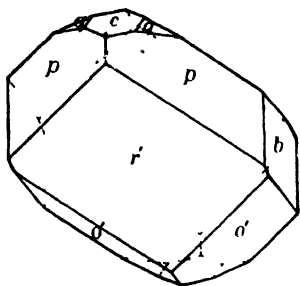
FIG. 21 —CRYSTAL OF AMMONIUM
FERROUS SULPHATE
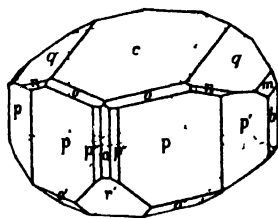
FIG. 22 —CRYSTAL OF POTASSIUM
NICKEL SULPHATE.

that the faces most extensively developed under ideal conditions of growth are those over which the points of the space-lattice are most densely strewn. Hence, von Fedorow tries to discover the faces of greatest reticular density by calculation. For it is a well-known fact that the most diverse habits —due to different faces being most prominently developed under different conditions of environment— are shown by the crystals of the same substance. A capital example is afforded by the double sulphates of the monoclinic series crystallizing with $6H_2O$. One of the commonest of these salts, ammonium ferrous sulphate, $(NH_4)_2Fe(SO_4)_2 . 6H_2O$, exhibits a particular form (consisting of a pair of parallel faces), $r'\{201\}$, not really a primary one, so prominently, the crystals being tabular upon it as illustrated in the lantern slide (Fig. 21), that Wulff has actually taken it as the basal plane, rather than the form $c\{001\}$, which is considered by the lecturer, following older observers, to be the true basal plane for this whole series of isomorphous salts. For the very large development

of r' is only a feature of this particular salt of a very large isomorphous series, and the form $c\{001\}$ is in general the plane clearly and prominently announcing itself as the basal plane. The slide (Fig. 22) of a crystal of another member of the series, potassium nickel sulphate, will show this. Hence, Prof. von Fedorow naturally does not rely on the fortuitous relative development of faces, but calculates the relative reticular density of all the principal faces present, in order to discover the true primary faces by their superior reticular density.

Having thus determined the correct setting, and measured the principal angles, including the five fundamental ones, the results are recorded in the index-table in an abbreviated symbolic form if the substance be a new one, or, if it has previously been measured and therefore appears in his index-table, he discovers the fact at once by the identity of the elements found with those of a substance given in the table. The average time occupied in all this by Prof. von Fedorow or one of his skilled assistants is about two hours. Mr. T. V. Barker, who studied with Prof. von Fedorow before acting as Demonstrator of Mineralogy at Oxford, has been of considerable help in submitting the new method to a very severe test, from which it has emerged with flying colours. He collected, at Prof. von Fedorow's suggestion, fifty specimens of substances which had been crystallographically examined in this country and described in the recognized publications. Five of these were furnished by the lecturer, six others by Prof. Armstrong with the aid of Messrs. Colgate and Rodd, others by Drs. Chattaway and Drugman, and Mr. Marsh at Oxford, and the remainder by Mr. Barker himself. Each specimen was only marked by a number, no name or formula being given, on its dispatch to St. Petersburg. The result was that Prof. von Fedorow identified without any difficulty 48 of the 50 substances. The crystals of one of the two others were too imperfectly developed to be of use, and the fiftieth specimen was that of a substance which it was afterwards discovered had never hitherto been measured, a fact which was first indicated by its elements not tallying with those of any substance mentioned in the table. This latter occurrence confers even greater confidence in accepting the new method.

It thus appears that in Prof. von Fedorow's hands, or those of his pupils, the method is practically infallible, provided the crystals are well developed and not of cubic symmetry. If the latter perfect symmetry be developed, reference must be made to the optical properties, which the lecturer has always insisted have been far too much neglected, and are here seen to be indispensable. The optical methods themselves, moreover, as regards their use with small crystals on the polarizing microscope, have been further perfected by von Fedorow, his Universal Stage placing the rapid methods of two- and three-circle goniometry at the disposal of the microscopist. It must also be remembered that Prof. von Fedorow's method does not discriminate between the members of isomorphous series, as the crystals usually

available are not of the high degree of perfection requisite in order clearly to substantiate the last few minutes of any particular angle ; for the differences of angle between the members of series formed by metallic family analogues have been shown by the lecturer to be very minute, although unmistakable given the most perfect crystals, and have also been found to obey the law of progression according to the atomic weight of the metal.   For instance, ammonium zinc sulphate was simply returned by Prof. von Fedorow as a member of the isomorphous series of monoclinic double sulphates and selenates crystallizing with $6H_2O$.   Qualitative analysis would be necessary after all, in order to discover the actual member of the series present.   Moreover, there are certain features of Prof. von Fedorow's own peculiar version of the theory of crystal structure, such as his idea about pseudo-cubic and pseudo-hexagonal types, and his dealing in consequence with many substances as being deformations of a higher symmetry than they actually show, which to the lecturer appear unnecessary complications likely to discourage the use of the new method   But these defects can, and doubtless will, be eliminated as the method becomes practically applied.

In conclusion, it must be obvious that a great advance has really now been made in crystallography.   For the geometrical theory of crystals as homogeneous structures, based on the 14 space-lattices as the grosser structures and the 230 point-systems as the ultimate atomic structures, has been not only theoretically perfected, but proved by direct experiment to be an actual fact, by the epoch-making work of Laue, Friedrich, and Knipping.   The descriptions and chemical relationships of all the ten thousand measured substances have been brought together in the great book of Prof. von Groth, and the material further sifted, reduced to correct setting, and arranged according to symmetry and elements by Prof. von Fedorow, in a tabular form immediately available as a reference index for identification purposes, thus providing the material for a true crystallo-chemical analysis.   The science of crystallography is thus now placed on a secure foundation, supported equally by mathematics, geometry, and experiment, and its natural data are rendered available for chemists and physicists alike.

It must be obvious that these significant results place the science in such a strong position that it can no longer be ignored as in the past by both physicists and chemists, and that to both an elementary knowledge of the subject will be imperative and absolutely indispensable in future.   That crystallochemical analysis will ever replace qualitative chemical analysis is neither to be expected nor desired, even if alone on the ground of the admirable training and experience in chemical operations and principles which chemical analysis affords.   But so powerful an aid cannot with impunity be neglected, and the knowledge of crystallography required of the chemist who desires to be armed with the new weapon of research

will be of the utmost benefit to him, in the sense of giving him a wider grasp of the nature both of the particular chemical solid matter under his own immediate investigation, and of the nature of solid matter, the most highly organized of all the forms of matter, in general.

[A. E. H. T.]

Appendix.

Since this lecture was delivered, the following further experiments with X-rays and crystals have been described in "Nature" (1912, Vol. 91, pages 111, 185, and 161). H. B. Keene has obtained with crystals of galena, mica, and rock salt analogous results to those of Laue, Friedrich, and Knipping, the spot diagrams corresponding to the holohedral systematic symmetry in each case. T. Terada has found that the transmitted rays may be rendered optically visible by means of an ordinary fluorescent screen, provided the pencil of rays be from 5 to 10 mm. in diameter and the crystal adequately transparent to the rays; this latter he found to be the case with crystals of alum, borax, cane-sugar, fluorspar, mica, rock crystal, and rock salt, in thicknesses of 4 to 10 mm. M. de Broglie has obtained spot diagrams similar to those of Laue, Friedrich, and Knipping, with fluorspar, magnetite (using an octahedron face), and rock salt; but all the spots were striated with parallel fringes. Finally, Owen and Blake have obtained what appears to be a line spectrum of X-rays by using the surface of a crystal of gypsum as a diffraction grating. The lines were always the same with different crystals, using the same X-ray bulb, but the different lines varied in intensity with the hardness (degree of vacuum) of the bulb. The evidence from the action of crystals on X-rays is thus accumulating that the X-rays are waves of exceedingly short wave-length. —A. E. H. T.

April 22, 1913.

The Spectroscope in Organic Chemistry.

SOMEWHAT more than half a century ago, while engaged, with the assistance of Faraday, in preparing experiments for a Friday evening discourse in this Institution, Stokes observed that the spectrum of the electric light extended to five or six times the length of the visible spectrum when he employed prisms and lenses of quartz instead of glass. This extension occurs at the violet end of the spectrum, and consists of rays of high refrangibility to which the eye is insensitive, but which can be made apparent by means of a fluorescent screen.

At the time of this discovery, and in the years immediately following it, attention was being directed to the absorption of light by coloured solutions, and to the possibility of identifying coloured substances by the number and position of the dark bands in the spectrum of light transmitted through their solutions. Stokes saw that by his discovery of the extension of the spectrum beyond the visible region, this method of investigation might be applied to colourless as well as to coloured substances. In a paper communicated to the Royal Society in 1862, he says :—" The mode of absorption of light by colourless solutions as observed by the prism, affords, in many cases, most valuable characters of particular substances, which, strange to say, though so easily observed, have till very lately been almost wholly neglected by chemists." . . . " Having obtained the long spectrum above mentioned I could not fail to be interested in the manner in which substances —especially pure, but otherwise imperfectly known organic substances—might behave as to their absorption of the rays of high refrangibility." He proceeded, therefore, to study the action of various organic solutions on the ultra-violet rays, and found that the mode of absorption generally was so constant and so characteristic that by this single property many substances could be identified. The substances which he examined included the best known vegetable alkaloids, all of which, with the exception of morphine and codeine, he was able to distinguish from one another by means of their absorption bands. This was a very remarkable anticipation of the results of later work on the subject, when we remember

the great difficulties that must have been encountered in observing and measuring accurately the position of bands on a luminous screen.

While Stokes was engaged in these researches, Prof. William Allen Miller was simultaneously at work in the same field, and Stokes left the further development of the subject in his hands.   Instead of a fluorescent screen, Miller employed a sensitive photographic plate for the reception of the spectrum.   The rays of light were by this means made to register their own position and intensity, and a permanent record was obtained which could be studied at leisure.   Miller failed, however, to " trace any special connexion between the chemical complexity of a substance and its diactinic power."   Struck by this fact, W. N. Hartley—now Sir Walter Hartley—commenced a systematic investigation of the whole subject, and it is to his researches, extending over a period of more than thirty years, that we owe, not only most of the knowledge which we now possess of the relation between the structure of organic substances and the action of such substances on the ultra-violet rays, but the elaboration of the convenient and elegant methods by which such investigations are now conducted.

The light derived from an ordinary source of illumination, such as an electric lamp, consists of waves of all degrees of refrangibility, and its spectrum shows a continuous band of colour ranging from red to violet.   The limits of this visible spectrum lie between the wave-lengths 7600 and 3900.

If, instead of the electric light or other ordinary source of illumination, we employ the light emitted by one of the metals when raised to a high temperature, the spectrum is seen to consist of a series of lines of different colours and intensities lying within the same limits as the visible spectrum.   But there are rays beyond the red end of the spectrum and rays beyond the violet end which excite no sensation of luminosity in the eye   By allowing the spectrum to fall upon a screen which has been coated with a fluorescent substance, such as sulphate of quinine or a salt of uranium, these rays are rendered visible for a short distance beyond the violet   But it is only when we replace the glass apparatus, with which we have hitherto been working, by a quartz prism and lenses, and substitute a photographic plate for the eye, that the full extent of the spectrum beyond the violet is revealed (Fig. 1).   This is the ultra-violet region —the region which Stokes opened up to investigation, and it is with the behaviour of organic substances towards the rays of this part of the spectrum that we have mainly to do this evening.

When light is transmitted through a coloured solution certain rays are absorbed, and dark bands corresponding to these rays appear in the spectrum   The importance of these bands as a means of distinguishing coloured substances has long been recognized, and, as we have already seen, considerable progress had been made with their study fifty years ago.   As the bands in this case are in the visible spectrum, no special means are required for their observation.
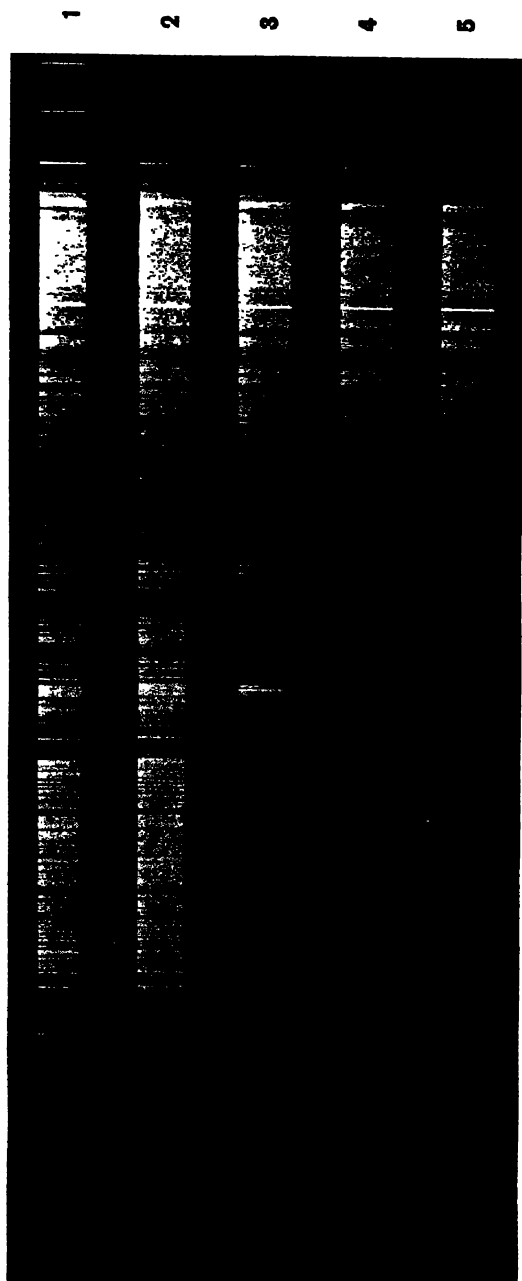
Fig. 1.

(1) Spark spectrum of nickel and iron; (2) the same after the light has passed through quartz 10 mm. thick; (3) crown glass 0·13 mm. thick; (4) crown glass 0·33 mm. thick; (5) window glass 1·62 mm. thick.

FIG. 2
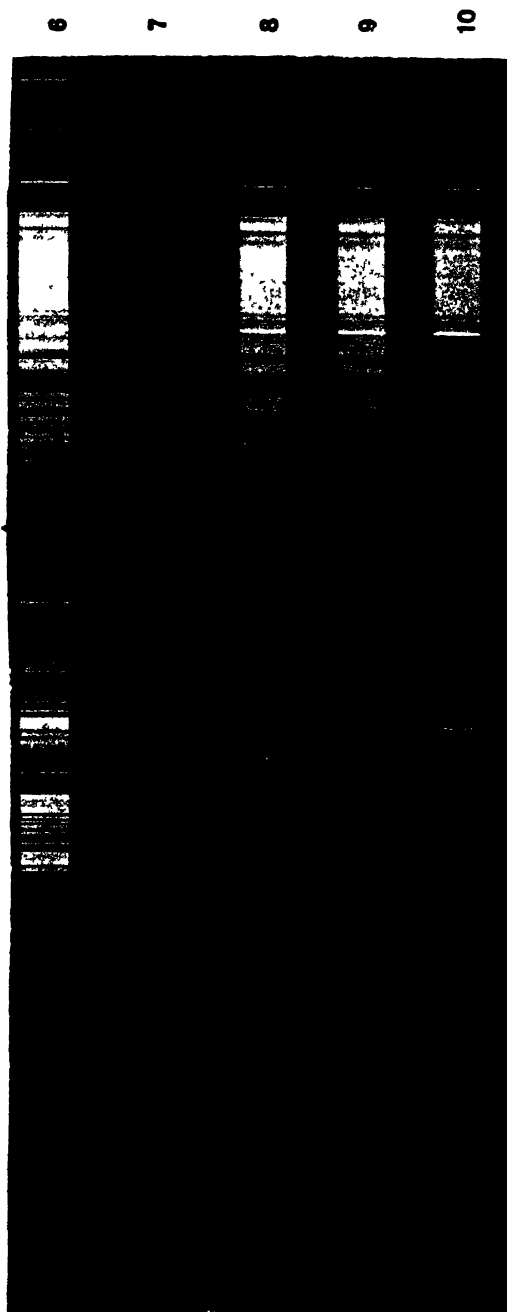
FIG. 2.

(1) Spark spectrum of nickel and iron; (2) and (3) the same after the light has passed through water and solution of cane sugar respectively; alcoholic solutions of (4) pinene (5) thiophen (6) citric acid (7) isatin (8) phenol (9) salicylic acid (10) quinine hydrochloride; (4) (5) and (6) illustrate general absorption; (7) (8) (9) and (10) illustrate selective absorption.
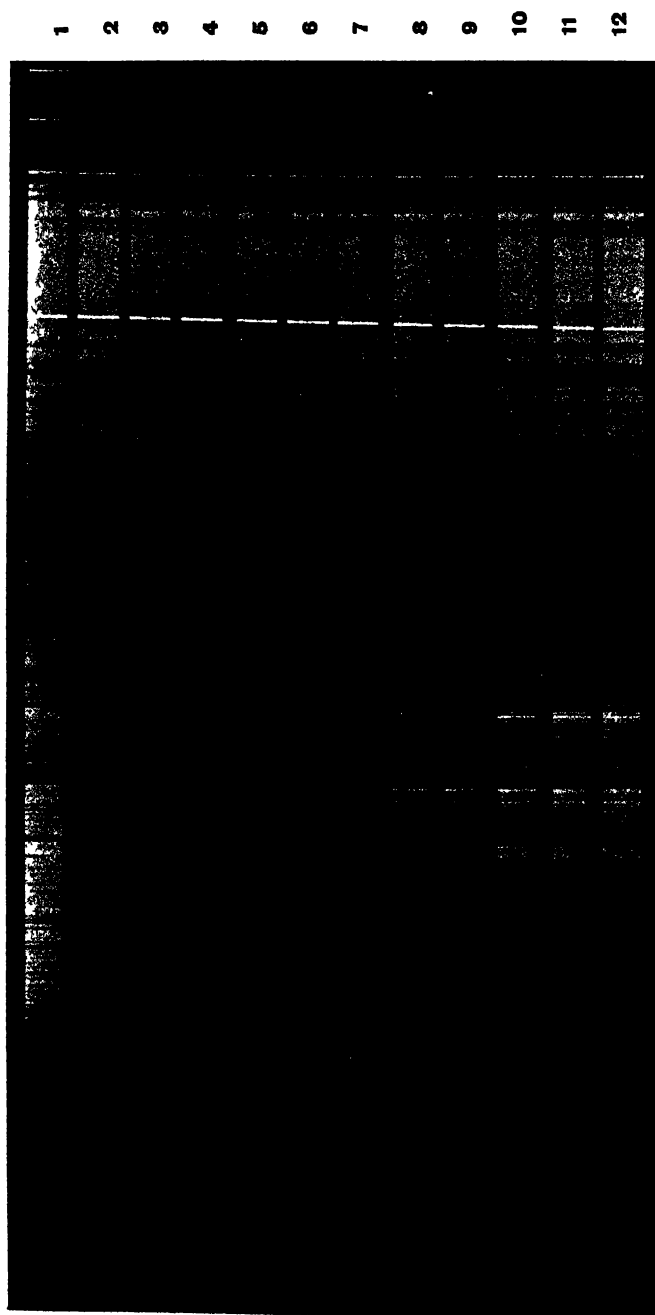
FIG. 3.

(1) Spark spectrum of nickel and iron   (2-12) the same after the light has passed through layers of 0·001 normal solution of salicylic acid from 90 to 4 mm thick

But when we extend this method of investigation to colourless substances, we are dealing with phenomena which lie hidden from the unaided eye, and our investigations are necessarily carried out with the help of photography.

The instrument employed in the study of absorption spectra consists of a spectroscope in which the eye-piece of the telescope is replaced by a camera. The photographic plate is set at such an angle as to bring all the rays emanating from the source of light into focus at its surface after they have passed through the resolving prism, and for this purpose it is necessary that the plate should have a very slight curvature. The prisms and lenses of the apparatus are made of quartz, which, unlike glass, is readily permeable by the ultra-violet rays. The source of light usually employed is that obtained by sparking one of the metals, such as iron, or a combination of metals, such as cadmium alloyed with lead and tin, selected so as to give a large number of lines spread as uniformly as possible over the whole ultra-violet region. The advantage of such a spectrum over a continuous spectrum is that the position of absorption bands, when they occur, can easily be determined with reference to the metallic lines whose wave-lengths and place in the spectrum are known with great accuracy. In using the apparatus a photograph is first taken of the spectrum of the source of light. A layer of the substance to be examined, which, if a solid, must be dissolved in a suitable diactinic solvent, such as alcohol or water, is then interposed between the source of light and the slit of the collimator, and another photograph is taken. By comparison of the two photographs it is seen what effect, if any, the substance has had upon the transmission of the light.

When organic substances are examined in this way it is found that some allow light to pass freely through them. Others shorten the spectrum by absorbing the rays at the ultra-violet end to a greater or less extent, and are said to show general absorption. Others, again, possess the remarkable property of absorbing rays of a particular wave-length, thereby producing gaps or bands in the spectrum; these are said to show selective absorption (Fig. 2).

In studying these phenomena in their relation to the chemical characters of a substance, it is of importance to determine not only the extent of the general absorption and the number and position of the absorption bands, but their degree of persistence, i.e. the range of concentration within which they are exhibited. It is necessary, therefore, to vary the concentration of the solution or the thickness of the layer so as to cover the whole phenomena of absorption. This is done by simply diluting the solution, or diminishing the thickness of layer on the one hand, until the entire spectrum is transmitted; and on the other hand, by increasing the concentration or the thickness of the layer until no further characteristic absorptive effect is produced. Photographs (Fig. 3) are taken at each

concentration, and a curve is drawn connecting the concentration and the absorption as measured with reference to the lines of the metal employed as a source of light. The values of the spectral lines are usually stated in wave-lengths, but in these curves it is preferable to express them in reciprocals of wave-lengths. It is also convenient to make use of the logarithms of the numbers representing the thicknesses of the layers examined, rather than the numbers themselves (Fig. 4.)

If we now enquire whether the substances which affect light in one or other of the different ways already indicated have themselves anything in common, we find that it is with those which possess the
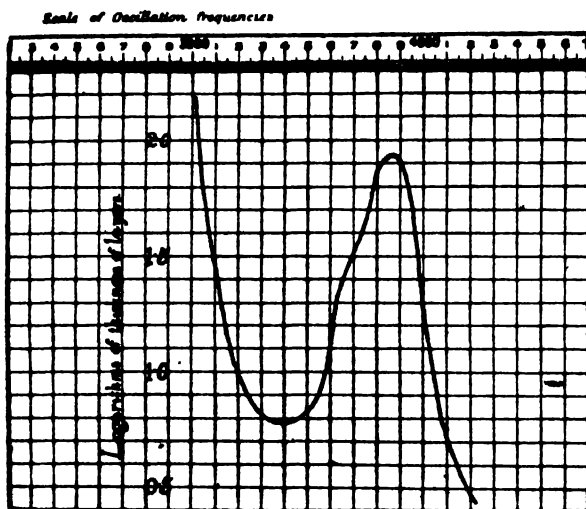
FIG. 4.—Salicylic acid 0·001 normal solution.

structure characteristic of benzene and its derivatives that the power of absorbing the rays of particular parts of the spectrum is most frequently, although not exclusively, associated

Organic compounds, or compounds containing the element carbon, are divided into fatty or aliphatic, in which the carbon atoms are united in an open chain, and cyclic, in which the carbon atoms form a closed chain or ring. Hexane, which is a constituent of liquid paraffin, may be taken as an example of the first class. This substance possesses six carbon atoms united together in a single chain and having attached to them fourteen hydrogen atoms, giving as the formula of the compound C_6H_{14}. This substance is highly diactinic or transparent to the ultra-violet rays, and nearly all compounds

belonging to the same division of organic chemistry such as alcohols, sugars, and fatty acids are either equally transparent to light, or only cut off a portion of the extreme ultra-violet rays of the spectrum.

If we now remove one atom of hydrogen from each of the two end carbon atoms of hexane, these atoms are in a condition to unite directly with each other, thus closing the chain. The substance so formed belongs to the cyclic division of organic compounds. It is known as cyclohexane, and has the formula C_6H_{12}, each carbon atom having two hydrogen atoms attached to it. This substance resembles hexane generally in its chemical properties, and behaves towards light in the same way, that is to say, it is practically diactinic or only cuts off some of the rays of light at the extreme ultra-violet end of the spectrum. Speaking quite generally, it may be said that bodies constituted like cyclohexane absorb more of the ultra-violet rays than those constituted like hexane.

But a wholly different condition is brought about if we suppose one atom of hydrogen removed from each of the six carbon atoms of cyclohexane. One linkage is thus set free in each of the six carbon atoms, and we obtain benzene. How these linkages are actually employed in benzene has never been determined with certainty. Sometimes they are represented as mutually neutralizing one another, sometimes as effecting a double link between the alternate pairs of carbon atoms. However this may be, the structure which bears the relation that I have indicated to the structure of hexane and cyclohexane is characteristic of the large group of organic substances of which benzene is the type. It is to this division of the cyclic compounds that the great majority of substances which show selective absorption, i.e. produce breaks or dark bands in the spectrum, belong. Here, then, we have a very important and a very general relation between the structure of organic substances and their absorption spectra.

The difference in the behaviour of organic bodies towards the ultra-violet rays, as exemplified in hexane and cyclohexane on the one hand, and benzene on the other, is brought out very clearly when we examine some of their derivatives. If we replace an atom of hydrogen in hexane or cyclohexane by the monovalent group hydroxyl, we get substances belonging to the class of alcohols, and these substances are, like their parent substances, highly diactinic. If, on the other hand, we replace an atom of hydrogen in benzene by the same group we get carbolic acid or phenol, which, like benzene, exercises selective absorption on the ultra-violet rays, but gives a spectrum widely different from that of benzene.

Having dealt with the most general relation that has been observed between the structure of organic substances and their action on the ultra-violet rays, I propose to illustrate some of the more special relations by examples from the phenomena of isomerism. By replacing an atom of hydrogen in carbolic acid or phenol by the nitro-

group we obtain three distinct nitrophenols. The ultimate particles or molecules of these nitrophenols are all composed of the same elements carbon, hydrogen, oxygen and nitrogen, and of the same number of atoms of each element. Such substances are said to be isomeric, i.e. they are made up of equal parts, although they do not possess the same properties. The difference between them lies in the arrangement of the parts relatively to each other; in this case in the position of the nitro-group in relation to the hydroxyl-group. On comparing the spectra of the three nitrophenols we find that they differ in quite a marked manner from one another, and afford an illustration of the important general rule that substances which have the same composition give different spectra if they differ in structure, i.e. in the arrangement of the atoms of their molecules.

It will have been noticed that the substitution of the nitro-group for hydrogen in phenol has the effect of shifting the absorption band nearer to the visible region. One of the three nitrophenols has a yellow colour, and in this case the gap in the spectrum cuts a little way into the violet end of the visible region. By the addition of soda to the solution the colour is changed to red, and on examining the spectrum of this solution we see that the gap now extends far into the visible region. This example will serve to illustrate the close connexion that exists between the study of absorption spectra and the origin of colour, an interesting branch of the subject with which, however, it is impossible for me to deal within the limits of this discourse.

In the nitrophenols we have an example of what is known as structural isomerism, or position isomerism, because the phenomenon depends upon differences in the position or arrangement of the atoms within the molecule—in other words, on the internal structure of the molecule. But it is possible to have two substances of the same composition and structure not identical, but related to one another as an object is to its mirror-image. Substances so related are termed optical isomers or stereo-isomers. The spectra of isomers of this class, unlike those of structural isomers, do not differ. This leads to an important application of absorption spectra in chemical investigations. If two substances have the same composition but different spectra, we know that they must be structurally different; if, on the other hand, they have the same composition and the same spectra, and yet are not identical, there is a strong probability, although not a certainty, that they are optical isomers. To take an example. We know three substances of vegetable origin—papaverine (from opium), canadine (from the roots of *Hydrastis canadensis*), and tetra-hydro-berberine (a derivative of the principal alkaloid obtained from species of the barberry)—which have the same chemical composition represented by the formula $C_{20}H_{21}NO_4$. Papaverine and canadine differ widely in their spectra and in their structure; canadine and tetra-hydro-berberine have identical spectra,

from which we should infer that they are in all probability stereo-isomers, a conclusion which has been independently established by the most satisfactory chemical evidence.

In applying this reasoning in the investigation of bodies of un-known structure, it has always to be borne in mind that while we may safely infer from dissimilarity of spectra, dissimilarity of structure, we cannot always infer similarity of structure from similarity of spectra.

The study of absorption spectra has proved of special value in the investigation of substances capable of existing in two forms which may pass from the one into the other. It is rarely the case that both forms of such substances are stable, and it is often extremely difficult, or altogether impossible, on account of this instability to determine by the ordinary chemical processes which of the two possible forms the substance as we know it possesses. Such substances, how-ever, frequently give rise to two series of stable isomeric methyl or ethyl derivatives, whose structure can be ascertained by chemical investigation. The parent substance, if not a mixture of the two forms, must correspond in structure with one or other of these derivatives, because it is a well-established fact that the introduction of the methyl or ethyl group into a substance in place of an atom of hydrogen does not appreciably alter the spectrum.

An example of this is afforded by the three substances isatin, methyl-isatin, and methyl-pseudo-isatin. The structure of methyl-isatin and of methyl-pseudo-isatin has been determined by chemical methods, but the structure of the parent substance isatin cannot be determined in this way. Is it constituted like methyl-isatin or like methyl-pseudo-isatin ? Inspection of the photographs of the spectra of the three substances shows that while there is a wide difference between the spectra of isatin and methyl-isatin, the spectra of isatin and methyl-pseudo-isatin are almost identical, as we should expect them to be on the view that they are constructed alike.

This phenomenon, which is known as tautomerism, is due to the fact that some substances contain an atom of hydrogen, or it may be a hydroxyl group, which readily shifts its position within the mole-cule, leaving its union with one atom to attach itself to another. Another example of this is afforded by cotarnine, a substance found in opium. The molecule of cotarnine possesses an atom of carbon which is directly combined with an atom of nitrogen, and has also united to it a hydroxyl group. Under the influence of certain reagents the hydroxyl group leaves the carbon atom and attaches itself to the nitrogen atom, but can readily, by an alteration of the conditions, be enticed back again to the carbon atom. The shifting of the position of the hydroxyl group is accompanied by other changes which, however, it is not necessary that we should take into account for our present purpose. In this case both of the tautomeric forms are, under certain conditions, stable. The form in which the hydroxyl is attached to the carbon is colourless, while the form in

which it is attached to the nitrogen is yellow.   The two forms have totally distinct absorption spectra.   When one of the forms passes into the other under the influence of the appropriate reagent, the amount of change is proportional to the quantity of reagent added. It is possible, therefore, by taking photographs after the addition of each successive quantity of reagent to trace the progress of the change through all its phases, and to ascertain how much of each form is present at any time.   This is done by comparison with a series of reference plates prepared by photographing mixtures in various definite proportions of two derivatives of cotarnine which possess the same spectra as the two parent forms.

Incidentally I may mention that these changes afford a basis for the measurement of the relative strength of alkalis and acids.   For example, the change from the yellow to the colourless form of cotarnine takes place under the influence of alkalis, and by comparing the amount of change produced by equivalent quantities of different alkalis we obtain a measure of their strength.

The spectrographic method of investigation has been applied with marked success to the study of the vegetable alkaloids.   Many of these substances, such as quinine, morphine, strychnine, and atropine, possess powerful and valuable physiological properties, and their careful investigation is of the greatest importance to medical science. The number of atoms present in the molecule of an alkaloid is nearly always large, frequently as many as fifty or sixty.   It is obvious, therefore, that the task of determining their exact relation to one another must be one of no little difficulty, and as a matter of fact the elucidation of the structure of an alkaloid is one of the hardest problems that the organic chemist can set himself.   Any method, therefore, which assists the chemical examination is of peculiar value in this branch of organic chemistry.

In investigating an alkaloid or any organic compound, the first thing that the chemist has to do is to determine the elements of which it is composed, and the number of atoms of each of those elements present in one of its molecules or ultimate particles ; in a word, what is known as its molecular formula.   This is a comparatively easy operation : the difficulty comes when he attempts to determine the structure of the molecule, i.e. the exact manner in which the atoms are arranged with respect to one another.   Now it may happen that two or more alkaloids have the same, or nearly the same, composition.   The question arises, are they constructed on the same plan ?   It is in attempting to answer this question that the value of the spectroscope asserts itself.   If on dissolving the alkaloids in some diactinic solvent and photographing their absorption spectra, we find that the spectra are wholly different, we may conclude that in spite of the similarity, or even identity in their composition, the substances are not intimately connected with one another.   If, on the other hand, we find that the spectra are the

same, or very similar, it is probable that the substances are closely related. If the composition is the same and the spectra are the same, the substances are almost certainly optical isomers. Of bodies related in this way we have already had an example in papaverine, canadine, and tetra-hydro-berberine.

Amongst the rare alkaloids of opium are two, to which the names of laudanin and laudanosin respectively have been given. They have nearly, but not quite, the same composition, laudanosin containing one atom of carbon and two atoms of hydrogen more than laudanin ; in other words, it is a homologue of laudanin. Substances so related, hardly differ in their spectra, the replacement of one atom of hydrogen by the group of atoms CH_3 having very little disturbing influence, as we have already seen, upon the structure of a substance or upon its power of absorbing light. The spectra of laudanin and laudanosin being practically the same, it was inferred that they possessed the same structure and were probably homologous, before the fact had been ascertained by the usual chemical examination.

I must here advert again for a moment to Stokes work on absorption spectra. I mentioned at the outset that he had been able to distinguish all the alkaloids he examined from one another by means of their absorption bands, except morphine and codeine. At that time the relation of these alkaloids to one another was unknown. We now know that they are homologues, and in that fact have the explanation of Stokes' failure to distinguish them by their absorption bands, and at the same time a striking testimony to the accuracy of his observations.

The examination of the spectra of laudanin and laudanosin not only revealed the fact that the two substances are homologues, but gave a clear indication as to the group of alkaloids to which they are most closely allied. When the spectra were compared with those of other alkaloids, they were found to resemble the spectra of cory- daline and the related alkaloids so closely as to leave very little room for doubt that they are built on the same plan as these alkaloids. At the time that this conclusion was arrived at, practic- ally nothing was known as to the chemical structure of laudanin and laudanosin, but the inference as to their close association with corydaline was subsequently fully justified by chemical investigation.

Apart from their structure there is another point of view from which the study of the spectra of the alkaloids is of interest and im- portance. These substances generally have very characteristic spectra by means of which they can be distinguished with certainty from one another, except when . they are homologous or otherwise very closely related. The spectroscopic method may, therefore, be used with great advantage in examinations for the presence of alkaloids to con- firm the results obtained by the usual chemical tests. The chemical tests are no doubt as a rule sufficiently distinctive, but considering the gravity of the circumstances under which they have frequently

to be applied, it is unnecessary to insist on the value of the confirmatory evidence which can be obtained by the use of the spectroscope.

The minutest quantities of alkaloids can be detected by this means, the method rivalling the colour reactions for the alkaloids in delicacy. Thus, with a quantity of strychnine not exceeding $\frac{1}{500}$ of a grain, a clearly defined spectrum of the alkaloid can be obtained. The photograph of morphine already shown was obtained with $\frac{1}{200}$ of a grain of the alkaloid (Fig 5), and that of nicotine with $\frac{1}{100}$.

The spectroscope serves not only for the detection, but for the estimation of alkaloids; by comparing the spectrum obtained with an unknown quantity of an alkaloid with a series of spectra obtained by photographing known quantities of the same alkaloid, it is possible to make quantitative determinations of a high degree of accuracy.

The use of the spectroscope in the detection and estimation of alkaloids in cases of poisoning, possesses certain advantages of the highest importance. One is that the material is not destroyed. The solution which has been employed for the spectroscopic examination can be used afterwards for the chemical examination. Another is that a permanent record is obtained which is always available for reference.

So far my illustrations have been confined almost entirely to colourless substances, because it is in connexion with the investigation of such substances that most of the recent advances in the subject have been made.

As my last example, I shall take the case of a coloured substance in which the method has been applied within the last year with marked success.

It will be remembered that considerable uneasiness was caused when it became known some time ago that nitrogen peroxide is sometimes employed to bleach flour. In the course of an enquiry into the subject, it became necessary to determine the nature of the colouring matter naturally present in flour. It was known that many of the yellow and orange pigments, so widely distributed throughout the vegetable kingdom, are either closely connected or identical with carrotene, the orange colouring matter of carrots, and it had been suggested that the colouring matter of unbleached flour might be identical with, or belong to the same class of colouring matters as this substance. It was impossible, however, to prove this by the usual chemical methods, because the amount of colouring matter in flour is so minute that its isolation in a pure state, and in sufficient quantity for chemical analysis, was hardly practicable. Carrotene, however, can be prepared in a pure state, and the happy idea occurred to Dr. Monier Williams, of the Local Government Board, who was conducting the investigation, to photograph its absorption spectrum and compare it with that of the colouring matter
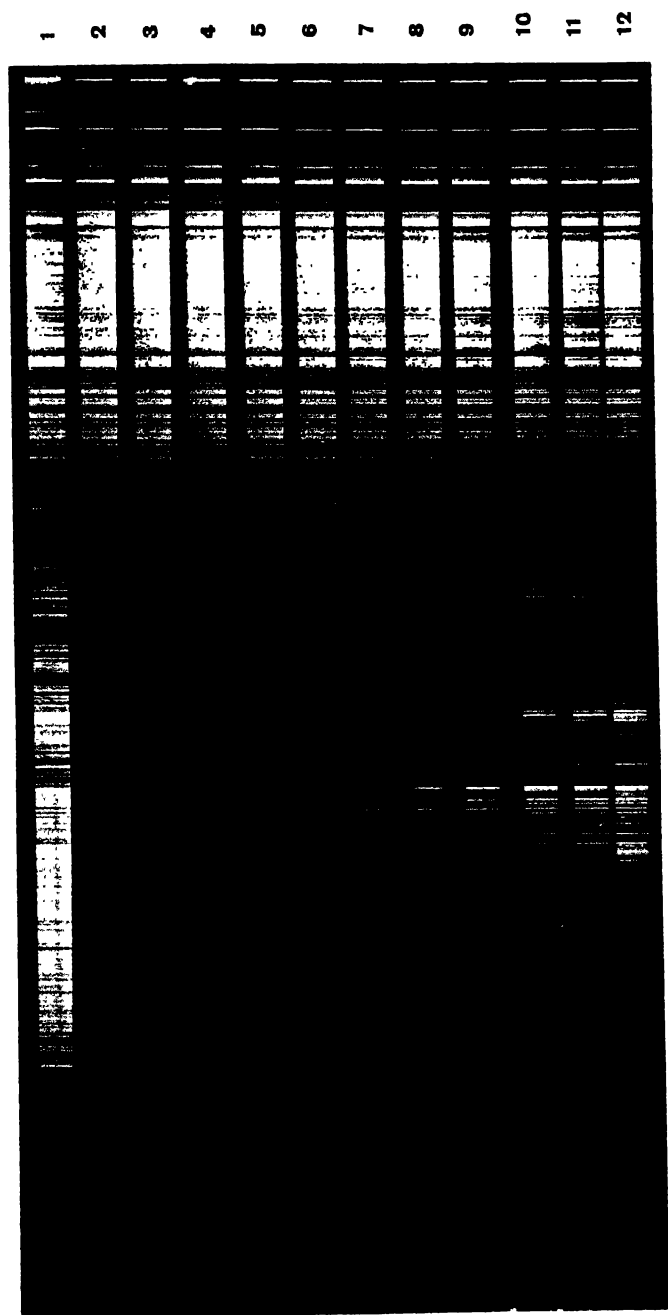
Fig. 5.

(1) Spectrum of nickel and iron; (2-12) the same after the light has passed through layers from 60 to 4 mm. thick of an alcoholic solution of morphine containing $\frac{1}{200}$ grain of the alkaloid.

of flour, which could easily be obtained in the minute quantity required for this purpose.   Inspection of the photographs shows that the spectra are very similar.   There cannot, therefore, be any doubt that the colouring matter of flour, if not identical with, is closely allied to carrotene.

The underlying causes of the relations between chemical structure and absorption spectra have been the subject of much speculation. Hartley considers that the phenomena of absorption are intimately connected with the vibration of the atoms within the molecule. This view has much to recommend it, but obviously its application is limited by the present imperfect state of our knowledge of the internal mechanism of the molecule. A theory has been advanced according to which absorption bands are only exhibited by compounds whose molecules are in a state of change or flux. In the case of ben-zene, for example, the old idea is revived that the carbon atoms are linked together by alternate double and single bonds, which are perpetually changing positions.   The presence of the bands in the spectrum of benzene, is supposed to be in some way connected with these changes.   Substances, however, are known which have banded spectra in regard to which such an explanation is inadmissible.

Quite recently a promising attempt has been made to bring the production of banded spectra into relation with the theory of electrons.

It must be confessed, however, that no satisfactory explanation of the phenomena of absorption has yet been formulated, and that the theoretical development of the subject lags behind its practical application.

[J.-J. D.]

Friday, April 18, 1913.

SIR FRANCIS LAKING, BART., G.C.V.O. K.C.B. M.D. LL.D.,
Vice-President, in the Chair.

THOMAS MARTIN LOWRY, ESQ., D.Sc. F.C.S.

Applications of Polarized Light.

ON November 30, 1812, just over 100 years ago, the French physicist
Biot communicated to the Institute of France a memoir "On a new
kind of oscillation which the molecules of light experience in travers-
ing certain crystals." In this paper, which extends over 371 pages
of the printed memoirs, the phenomenon of "Rotatory Polarization"
was described for the first time. This phenomenon, as most of you
will be aware, depends on the property which certain substances
possess of taking a beam of polarized light and imparting a twist to
the plane of polarization : the beam of light enters with all the
vibrations compressed, say, into a vertical plane ; it emerges
apparently unchanged, but careful examination shows that the com-
ponent vibrations are no longer vertical, but inclined either to the
right or to the left. The importance of this discovery to physicists
and to crystallographers was immediately obvious. In our own
generation its fertility has been realized also by chemists, who have
found in the polarimeter an instrument which promises to render
to the science services not less notable than those which have been
accomplished with the help of the spectroscope.

A.—SOURCES OF POLARIZED LIGHT.

If one were to ask what progress has been made in the facilities
for applying polarized light to the study of chemical and physical
problems, the answer would be two-fold. On the one hand it must
be acknowledged that the "Iceland spar," by means of which
Huyghens in 1678 first detected the polarization of light, is still the
best substance for producing this effect. But the increasing demand
for the spar has not been accompanied by any corresponding increase
in the supply, and large clear pieces of the mineral are becoming
increasingly difficult to procure. It may indeed be doubted whether
large polarizing prisms such as those which have been handed down
as heirlooms at the Royal Institution could now be purchased at any

price, in view of the "spar-famine" which has prevailed for some years.

Considerable advance has, however, been made in the direction of improved methods of illumination. The solar light, which figured so largely in the experiments of the earlier workers, is too precarious to satisfy the ardent worker of to-day, and in any case could render no direct assistance in illustrating a Friday Evening Discourse.

When Faraday on Friday, January 23, 1846, delivered his discourse on "The Magnetization of Light" to an audience of 1003 persons, the source of light in the experiments which he described was an Argand gas-burner. Professor Silvanus Thompson in 1889 was able to use the electric arc, which was then just beginning to come to the front as a commercial illuminant. With this unrivalled source of light he was able to show for the first time in a public lecture a large number of the properties of polarized light which had been reserved hitherto for individual observation in the laboratory.

The remarkable effects which are seen when light of one single colour or wave-length is substituted for white light were shown by Spottiswoode in 1878, with the help of a powerful sodium-lamp which had been devised by Sir James Dewar. His lecture was aptly described as "A Nocturne in Black and Yellow."

During several years I have taken a special interest in seeking to discover other sources of monochromatic light for use in experiments on polarization, and have been particularly concerned to proclaim the merits of the mercury arc as an illuminant for everyday use in optical investigations. On account of the predominance of three pure colours, the few experiments with the mercury arc, which I hope to show you this evening, might perhaps be described as a "Pastoral in Yellow, Green and Violet."

THE MERCURY ARC.

The spectrum of the light produced by passing an electric discharge through mercury vapour was described by Wheatstone in 1835 in a report to the British Association "On the Prismatic Decomposition of Electric Light"; but it was not until twenty-five years later that a real mercury-lamp was invented by Professor Way. This consisted of an intermittent jet of mercury which was directed into a cup half an inch below. The current from a battery of Bunsen cells was passed through the jet and developed an intense light. The spectrum of the light was examined by Dr. J. H. Gladstone, and described in a paper "On the Electric Light of Mercury," published in the 'Philosophical Magazine' of 1860 (Vol. XX. pp. 249–253).

The first use of the mercury arc as a source of light in polarimetry appears to have been made just ten years ago by two German workers, Disch and Schönrock, working independently (Disch, Ann.

Phys. 1903 (IV), Vol. XII. 1155 ; Schönrock, Zeit. Vereins Deutsch. Zuck. Ind., Tech. Part, 1903, Vol. LIII. 652). Through the personal kindness of Mr. Bastian, 1 was enabled about three years later to make use of the same source of light in what is still, perhaps, its most convenient form. The glass Bastian lamp was designed to burn with the coils of the arc in a horizontal plane, and was arranged to light automatically in this position. It was with great delight, therefore, that I discovered that, in spite of all warnings to the contrary, the lamp would continue to burn for any length of time with the coils raised into a vertical plane ; in this position one of the straight portions of the arc could be focused by a condenser directly on to the slit of a spectroscope, and so used to illuminate the field of a polarimeter. The lamp consumed very little current, and could be connected directly to the ordinary lighting circuits without any risk of " blowing " the fuses ; it was cheap to purchase, and as the resistances formed part of the holder of the lamp there was no need for any auxiliary apparatus whatever. In view of its special suitability for polarimetric work, it is to me personally a matter of some regret that this pioneer lamp has been displaced completely by the more powerful arcs, encased in refractory silica glass, which now adorn the exteriors of so many places of amusement. I use the word " exteriors " advisedly. Dr. Gladstone in 1860, in describing the properties of the mercury light, " was struck by the strange manner in which it modified the apparent colours of surrounding objects, and especially with the ghastly purple and green hues which it imparted to the faces and hands of the spectators." These green and purple hues would not be likely to find favour with a modern audience, and it is therefore not surprising that this powerful and economical lamp is more valued as a source of light for factories and dockyards than for exclusive use in lecture theatres and drawing-rooms.

When using the mercury arc as a source of violet light, account must be taken of the greatly reduced sensitiveness of the eye to light of such short wave-length. It is here that the silica mercury lamp has proved of such great utility. I am indebted both to Mr. Lacell, of the Silica Syndicate, and to the Brush Electrical Engineering Company for allowing me, for experimental purposes, to distort their well-considered designs for commercial mercury arc lamps. Here, for instance, is a horizontal lamp which has been altered so that the arc can be seen at its greatest intensity in an end-on position. At first the light was liable to be obscured by globules of condensed mercury. But by recessing the window it was kept sufficiently hot to prevent condensation, and this difficulty was effectively overcome. Even then, however, the arc was not so convenient as one arranged in a vertical plane, like the upturned Bastian lamp. It was at this stage that I persuaded the Brush Company to modify for me their " Quartzlite " lamp by twisting one of the terminal U-tubes into such a position that it did not empty itself when

the lamp was raised into a vertical plane.   The " end-on " lamp and the vertical Quartzlite lamp have been described in the Transactions of the Faraday Society (1912, vol. VII. pp. 267–270), and were exhibited at the Optical Convention of June 1912.   The lamp which I am using to-night has not been described previously.   It combines the merits of both of the preceding patterns, and can be used either horizontally or vertically, and either in a side-on or in an end-on position.

THE " PINCH EFFECT."

One feature of the silica mercury-lamps is sufficiently remarkable to deserve attention.   When the arc is first struck by tilting the lamp it fills the whole of the bore of the half-inch tube which encloses it ; but, in accordance with Faraday's observation that currents travelling in the same direction attract one another, the parallel threads of current are drawn together until finally, as you see, the arc is " pinched " together into a thread occupying only about one-third of the diameter of the tube.   This pinching together of the arc contributes substantially to its efficiency as an illuminant in polarimetric and spectroscopic work, and enables me to-night to use the arc as a linear source of light without introducing any auxiliary slit.   The shape of the arc is, however, altogether unsuitable for projection, which demands, as a condition for successful work, a powerful point-source of light.   I must therefore apologize for the small scale on which I have been obliged to project my illustrations, and should like to add that even these imperfect experiments have only been rendered possible by using the enormous Nicol prisms bequeathed to the Royal Institution by Warren de la Rue and by William Spottiswoode.

FIG. 1. — MERCURY LAMP FOR USE IN A HORIZONTAL OR VERTICAL SIDE-ON OR END-ON POSITION.

If the current in the mercury arc is increased, the pinching effect may extend to the point of breaking the threads of current completely and so extinguish the arc.

It may be of interest to some if I refer here to the well-known fact that the " pinch effect," which I have exhibited on a small scale in one of these tiny mercury-lamps, is of great importance in the electrical melting of steel on a large commercial scale.   In that case

Yellow ${5790\ 49 \atop 5769 \cdot 45}$

Green — $5460 \cdot 97$

Violet — $4356\ 58$ with two satellites

Deep Violet — $4078\ 03$ $4046\ 78$

Ultra-violet
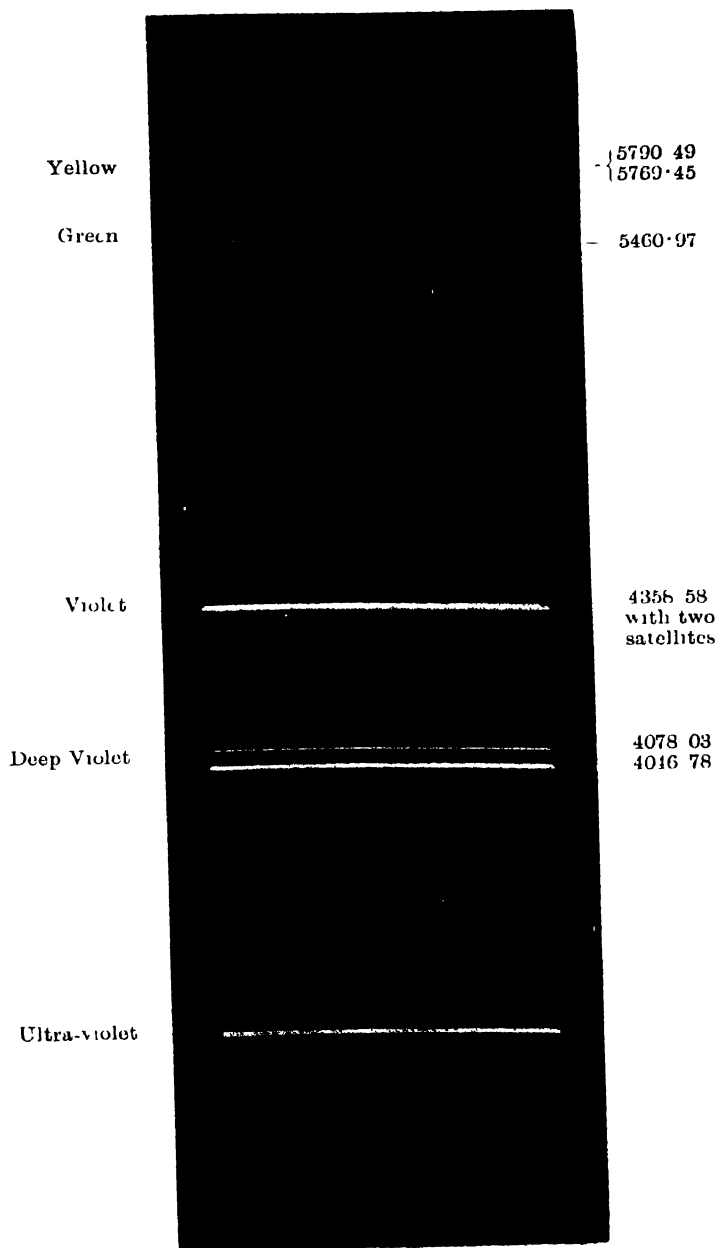
FIG 2.—THE VISIBLE SPECTRUM OF MERCURY.
(*By courtesy of Messrs. A. Hilger, Ltd.*)
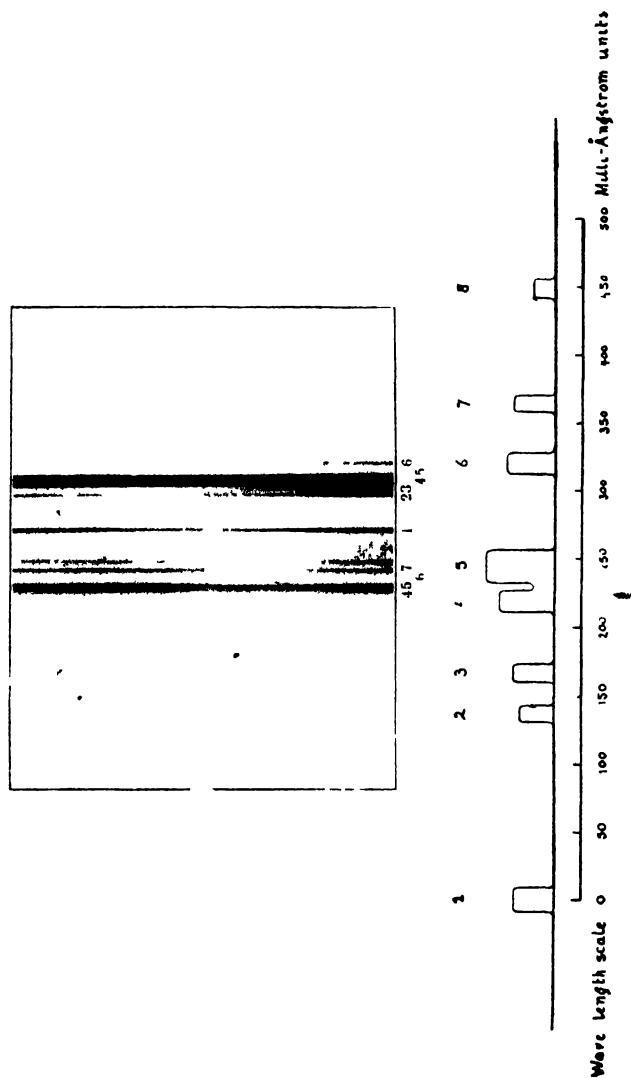
FIG. 2.—RESOLUTION OF THE MERCURY GREEN LINE BY THE ECHELON SPECTROSCOPE
The actual distribution of the components is shown by the diagram

b courtesy of Professor Strutnald

a current of great magnitude, flowing through a mass of molten steel enclosed in a circular channel, sometimes causes the metal to pinch together to such an extent that the circuit is actually broken. The "pinching" apart and running together of the mass of molten metal, which may weigh as much as three or four tons, produce a somewhat thrilling display.

The Mercury Spectrum.

The mercury arc differs from the carbon arc in giving an extremely simple line-spectrum, the chief features of which are a yellow, a green, and a violet component. The yellow component contains two lines, separated by about 20 units of wave-length as compared with six units for the yellow sodium doublet; it shows up well in the spectrum, but on account of its duplex character it is not suitable for use in exact measurements.

By means of powerful high-resolution apparatus, such as the echelon spectroscope, the green line of the mercury spectrum has also been shown to be complex; but in this case the components are so close together that they do not in any way reduce the value of the line as a source of monochromatic light. The extreme brilliance of this green line, its high spectroscopic purity, and the ease with which it can be produced, have given to it an unrivalled position amongst the various sources of monochromatic light which are now available for polarimetric work. I can say with confidence that no one who has worked with the mercury lamp will ever wish to return to the sodium flame, which it is rapidly displacing both in scientific and in technical laboratories.

Dr. Gladstone directed special attention to the strength of the violet lines in the spectrum, of one of which he said that "this ray is situated far beyond what is ordinarily considered the limit of the luminous spectrum." This deep-violet component contains two lines which are clearly visible in the spectroscope; but they lie so near to the limit of visibility that their presence can be shown most clearly with the help of a fluorescent screen. The bright violet line is, from the scientific point of view, one of the most valuable features of the mercury spectrum. The main line is accompanied by two satellites of greater refrangibility; but these are so close to the principal line, and are of so much smaller intensity, that they do not diminish appreciably the unique value of this line, which still remains the most powerful source of monochromatic light for work at the violet end of the spectrum. Actual measurements in which the violet line has been used both with and without the satellites have shown that the errors introduced by the presence of the latter do not exceed one part in 10,000 on the readings of a polarimeter. This error would, therefore, be quite inappreciable in the case of all readings of less than 100°.

The spectrum that I have shown to you does not by any means

exhaust the usefulness of the mercury arc. In addition to the lines of the visible spectrum, there is a powerful series of ultra-violet lines which are freely transmitted by the glass of the silica lamps. These are of value for a number of scientific purposes, and have found an important technical application in the sterilization of water.

To touch on a subject that is perhaps less generally familiar, I have found that, on the other side of the spectrum, the magnificent though invisible line at wave-length 10,140 is of unique value as a starting point for calibration work in the infra-red. It will also be remembered that some of the longest waves of light that have yet been detected were discovered by Rubens in the radiation from a mercury lamp.

RESOLUTION OF THE MERCURY SPECTRUM.

One merit of the mercury arc as a source of light consists in the readiness with which the three main components may be separated. A direct vision prism of quite moderate dispersive power, placed in front of the eye-piece of a polarimeter, produces a separation of the three images which is sufficient for most purposes. The lines may also be separated by means of coloured screens prepared from gelatine films stained with suitable dyes. The efficiency of these screens may be shown by interposing them one by one in the path of the beam which forms the images which are now thrown on the screen. The lines selected for transmission are weakened in intensity, but the others are absorbed so completely that the transmitted light can be obtained spectroscopically pure.

Occasionally it is desired merely to reduce the glare of the green line in order to render the violet line more distinctly visible. An ideal dye for this purpose, which was suggested to me a year ago by Dr. Mees, is xylene red.

This substance fluoresces so beautifully under the light of the arc that I cannot resist the temptation to show it to you in the striking form which Sir James Dewar has used to exhibit this effect in the case of other dyes.

If I have dwelt at some length on the merits of the mercury arc, I may perhaps be excused on the ground that to one's scientific colleagues the description of a novel tool, which they may be able to use in their own work, is usually of greater interest and importance than any record of the work for which it may already have been used.

B.—ROTATORY POLARIZATION.

The phenomenon of rotatory polarization was first discovered in the case of quartz. Arago in 1811 (Mem. Inst., 1811, pp. 93–134) found that a plate of quartz interposed between a polarizer and analyser was capable of depolarizing the light in such a way that transmission took place where previously there had been complete

— 2378 4

— 2446 9
— 2464 1

— 2576·3

{ 2652 2
2653 8
2655 4

— 2752·9

— 2893 7
— 2925 5

{ 3125·8
3131 6
3131 9

— 3390 5

{ 3650 3
3655 0
3663 5

4046 7
4078 0

— 4358 0

— 4916 4

5460 7
— { 5769 6
5790·5
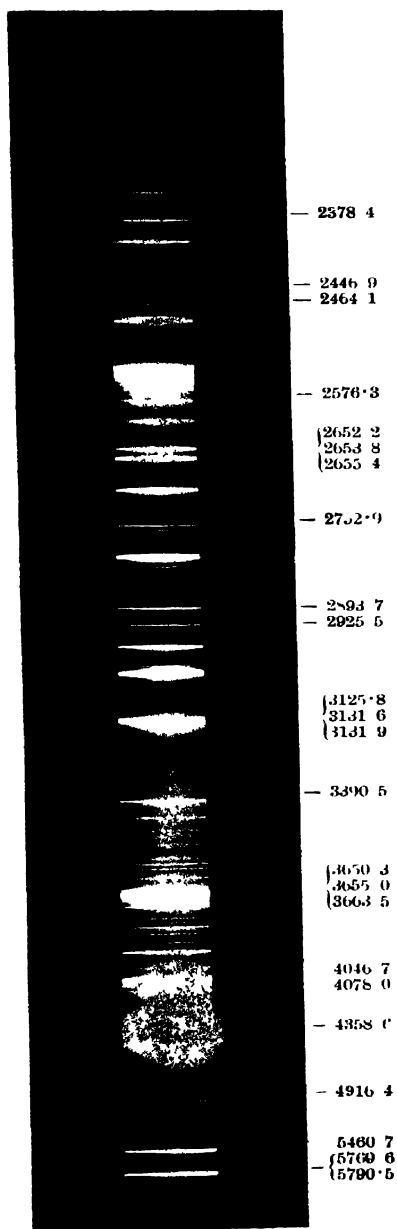
FIG. 4.—THE ULTRA-VIOLET SPECTRUM OF MERCURY.
(By courtesy of Messrs. A Hilger, Ltd)

extinction. When plates of suitable thickness were used the trans-
mitted light was no longer white, but beautifully tinted, the colour
of the light varying with the thickness of the plate. Thus with
increasing thickness we have progressively yellow, orange, rose-red,
violet, blue, and green.

These colours were shown by Biot to be due to a rotation of the
plane of polarization, which increased (A) with the thickness of the
plate, (B) with change of colour from red to violet. It is therefore
impossible when a beam of polarized light has passed through a
quartz plate to extinguish all the colours simultaneously.

The tints which Arago observed were due to the selective ex-
tinction of light of different colours by the mirror which he used as
an analyser. This selective extinction may be shown by inserting a
direct vision spectroscope in front of the apparatus : the plate which
produces the pale yellow colour has rotated the violet light through
180°, so that it is extinguished exactly as if no quartz plate were
present ; the yellow tint is the complementary colour to that ex-
tinguished. As the thickness of the plate increases, the same effect
is produced with light of longer wave-length ; as the extinction
moves from violet to red the complementary colour changes from
yellow to orange, red, blue, and green. When the bright yellowish-
green is extinguished a grey "neutral tint" is produced which is
extremely sensitive to small rotations of the plane of polarization,
and was at one time used very largely in polarimeters illuminated
with white light.

When the mercury arc is used as a source of light, the colours are
mainly two—green and violet ; but the violet colour, especially, is so
beautiful that I cannot refrain from showing you a few of Spottis-
woode's experiments as they appear when the light of a mercury arc is
substituted for the white light which he used in illustrating his
Friday evening discourses.

When monochromatic light is used—as, for instance, when a green
screen is placed in front of the mercury arc—the light can be extin-
guished completely even after it has passed through a very long
column of quartz. Using green light purified by a spectroscope and
rods of quartz cut from a crystal of extraordinary beauty, I have
obtained a perfectly sharp extinction with a column of quartz half a
metre in length, giving an actual rotation of $12,789 \cdot 20° \pm 0 \cdot 01°$.
I have also been making experiments with the same material to
determine accurately what rotation is produced by quartz in light
of different wave-lengths, not only in the visible spectrum, but also
in the infra-red and ultra-violet regions ; but as the work is still
incomplete, I will not attempt to describe it, but pass on at once to
other ways in which rotatory polarization may be produced.

Three years after his discovery of rotatory polarization in quartz,
Biot was astonished to find that the same property was possessed
by certain liquids, turpentine and laurel-oil rotating the plane of

polarization to the left, and oil of lemon and camphor (dissolved in alcohol) rotating it to the right.

In the case of quartz, Biot had attributed the rotation of the plane of polarization to the crystalline structure of the material.* The correctness of this view was proved when it was shown that rotatory polarization no longer took place when the crystalline structure of quartz was destroyed by melting it or by dissolving it in alkali. In the case of liquids this explanation was no longer possible. Rotatory polarization must here be attributed to some lack of symmetry in the structure of the molecule rather than of the crystal. It is in such cases that the polarimeter has proved its supreme value in the investigation of molecular structure. In this connexion it will be sufficient if I refer to the classical researches of Pasteur, van't Hoff, and le Bel, and to the brilliant contemporary work of Pope, Kipling, Smiles, and Mills in our own country, and of Meisenheimer and Werner on the Continent. In each of these investigations the development of " optical activity " has been accepted as a conclusive proof of molecular asymmetry, and no firmer basis for theories of molecular structure has yet been found than that which rests upon the use of the polarimeter to detect rotatory polarization.

I should have liked, if time had permitted, to refer to Faraday's discovery of the rotatory polarization induced in inactive substances, such as glass and water, by exposing them to the influence of a powerful magnetic field. I had also hoped to be able to demonstrate this phenomenon in one of the pieces of heavy glass prepared by Faraday himself, using for this purpose the large electro-magnet employed by the late Sir William Perkin in his investigations. But a passing reference to this third method of producing rotatory polarization is all that is possible to-night.

C.—MUTAROTATION.

In 1846, thirty years after Biot had discovered that rotatory polarization might occur in liquids as well as in crystals, a remarkable discovery was made by the French chemist Dubrunfaut in reference to the rotatory power of aqueous solutions of grape-sugar or glucose. Dubrunfaut found that by using freshly-prepared solutions of the sugar he could observe a transient rotatory power which was twice as great as that observed in solutions which had been prepared a few hours previously. To this remarkable phenomenon he gave the name Birotation.

The same phenomenon, which is now generally known as Muta rotation, has since been observed in the case of nearly all the

* In associating rotatory polarization with double refraction, he was wrong, as crystals of sodium chlorate, which show no double refraction, are still capable of rotating the plane of polarized light.

" reducing " sugars. Many explanations were given to account for so mysterious a change, but nothing in the way of proof could, as a rule, be offered in support of these suggestions. In 1890, however, Emil Fischer discovered that similar changes of rotatory power occurred when gluconic lactone was dissolved in water and thus partially hydrolysed to gluconic acid—

$$C_6H_{10}O_6 + H_2O \; \rightleftarrows \; C_6H_{12}O_7$$
Gluconic lactone   Gluconic acid.
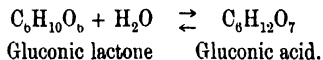
He therefore suggested that a similar explanation might be given of the mutarotation of glucose, thus—

$$C_6H_{12}O_6 + H_2O \; \rightleftarrows \; C_6H_{14}O_7$$
Glucose   Glucose hydrate.
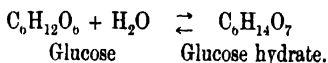
MUTAROTATION OF NITROCAMPHOR.

In 1896 a happy accident led me to the discovery that very marked changes of rotatory power occur in freshly-prepared solutions of nitrocamphor. But, unlike the case of glucose, these changes could be observed in a large range of solvents. The change varied greatly in the numerical values involved, but was always in the same direction—from left towards right.

The cause of the mutarotation was not difficult to discover. It could not be due to hydration, nor indeed to any direct chemical action of the solvent, but must be attributed to some change of structure in the molecule of the nitrocamphor itself. In view of the fact that the nitro compound is able to simulate the properties of an acid, giving rise to strongly dextrorotatory salts, there could be little doubt that the change of rotatory power was caused by a partial conversion of the nitrocamphor into its acidic form—a conversion which can be rendered complete by the addition of alkali. This view was immediately confirmed by the discovery of a dextrorotatory anhydride, which could be prepared from nitrocamphor merely by evaporating its solutions on a water-bath.

This interconversion of isomeric compounds, which we have called Dynamic Isomerism, could also be used to explain the mutarotation of glucose, of which two isomeric forms are known ; but there is good reason to believe that the hydrolysis suggested by Fischer is also an important factor when aqueous solutions of the sugar are under consideration.

In the case of bromonitrocamphor two isomeric forms of the substance can actually be isolated, thus affording direct evidence that the mutarotation observed in the case of this compound is due to a reversible isomeric change.

FORM OF THE CURVES.

In most cases the change of rotatory power proceeds according to a very simple law, the rate of change being directly proportional to the distance still remaining to be traversed.

But I have recently found a number of cases in which the curves are far more complex. In such instances it is necessary to assume a series of successive isomeric changes; but this assumption presents no difficulty, as the substances in question can all be formulated in at least five different ways.

ACCELERATION BY CATALYSTS.

The mutarotation of glucose is accelerated to a moderate extent by acids and very largely indeed by alkalis. Similar observations have been made in the case of nitrocamphor. Piperidine added to a solution of nitrocamphor in benzene produces a remarkable acceleration which can be detected even at a concentration of $N/10,000,000$, i.e. 1 part in 100 million or 1 centigram per ton. Aniline is 100,000 times less active.

ARREST OF ISOMERIC CHANGE.

The fortunate selection of chloroform as one of a series of solvents led to the discovery of one of the most important facts that has come to light in the course of fifteen years' work on mutarotation. In the very earliest stages of the work it was found that solutions in chloroform behaved in a very irregular and surprising way; the mutarotation in this solvent seemed sometimes to " hang fire " until set going by some accidental stimulus. These observations were evidently important as proving that isomeric change was not spontaneous, even after the nitrocamphor had been dissolved. But for ten years no explanation was forthcoming to show why this phenomenon was observed in chloroform, and in chloroform only. About five years ago, however, an arrest of isomeric change was again observed in the case of chloroform solutions to which a trace of acid had been added. These solutions (the rotatory power of one of which " held up " absolutely during twenty-four days) acquired a pungent and horrible odour, and had evidently undergone marked decomposition. It was not long before the odour was recognized as being due to carbonyl chloride—a well-known and (in anæsthetic chloroform) a dangerous impurity, formed by oxidation of the chloroform according to the equation $CHCl_3 + O = COCl_2 + HCl$. This substance has the property of attacking ammonia and organic bases such as piperidine and converting them into neutral ureas, as shown by the equations :

$$COCl_2 + 2NH_3 = CO(NH_2) + 2HCl$$
$$COCl_2 + 2NC_5H_{11} = CO(NC_5H_{10})_2 + 2HCl.$$
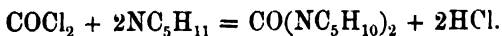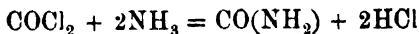
The next step was obviously to try to arrest the isomeric change by the addition of carbonyl chloride to a solvent which did not naturally contain it. This was done with marked success. A solution of nitrocamphor in purified ether showed a change of rotatory power extending over about a day; by the addition of carbonyl chloride the period was increased to eighteen days in a glass vessel, and to sixty-one days when a silica vessel (free from alkali) was used to contain the solution. In the case of benzene, to which acetyl chloride was added, the period was increased from sixteen days to sixty-four days in glass, and to two years in a silica vessel. Finally, by the addition of carbonyl chloride to a solution of nitrocamphor in benzene contained in a silica vessel the period was increased from sixteen days to six years.

ACTION OF LIGHT.

A convenient method of studying the effect of light on isomeric change has recently been devised in which the polarimeter plays a leading part. The solution to be studied was enclosed in a silica tube, surrounded by a silica water-jacket, and exposed to the light from a silica mercury lamp. In seven cases out of nine, however, no acceleration whatever could be detected as a result of this extremely powerful "insolation."

I have attempted to give some account of a few instances in which polarized light has been applied to the solution of chemical and physical problems. In each case the observations have taken the form of measurements of rotatory polarization. Measurements such as these have supplied to the chemist a key which has enabled him to unlock the strong-room in which many of the secrets of molecular structure were stored. The physicist, too, following in the footsteps of Faraday, has found in rotatory polarization a link between the sciences of magnetism and optics, and has obtained valuable hints as to the way in which light is propagated through matter. The hundred years which have elapsed since Biot announced his great discovery have therefore served only to enhance its brilliance, and to reveal it as one of the most illuminating disclosures even of the splendid period in which it was made.

[T. M. L.]

Friday, January 23, 1914.

SIR JAMES CRICHTON-BROWNE, J.P. M.D. LL.D. D.Sc. F.R.S.,
Treasurer and Vice-President, in the Chair.

PROFESSOR SIR JAMES DEWAR, LL.D. D.Sc. F.R.S. *M.R.I.*,
Fullerian Professor of Chemistry, R.I.

The Coming of Age of the "Vacuum Flask."

TWENTY-ONE years ago the application of vacuum jacketed vessels to the storage and manipulation of liquefied gases or for conserving hot liquids was made in the Laboratory of the Royal Institution. Such vessels are now popularly called "Thermos Flasks." The insulating properties of a vacuum in preventing the influx of heat by the elimination of convection currents had been known to physicists ever since the investigations of Dulong and Petit on the laws of radiation, in the early part of the last century, proved the important part played by the gas particles surrounding a body in dissipating heat, otherwise than by pure radiation. As far back as 1873 a highly exhausted annular metallic vessel was used by the lecturer in calorimetric experiments described in my paper on "The Physical Constants of Hydrogenium." * This naturally suggested that the use of high vacua in the annular space surrounding vessels containing liquid gases would be advantageous. The experiments which led up to the use of glass vessels isolated by a vacuum space are fully described in the Friday Evening Discourse on January 20, 1893.† Some of the early forms of vessels then described are shown in Fig. 1.

One of the primary difficulties was connected with the construction in glass of concentric spherical or cylindrical vessels that would withstand the atmospheric pressure, and bear considerable oscillations of temperature without cracking. This was a serious impediment which was only gradually overcome by the growing demand and by improvements in the blowing and adequate annealing of the glass : some of the various developments of form rising out of the needs of low temperature research are figured in the abstract of the Discourse of January 18, 1901, which is now reproduced.

A sufficient vacuum can be obtained with the ordinary Sprengel pump. Glass flasks so exhausted were quite satisfactory for heat

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* Trans. Roy. Soc. Ed. xxvii. p. 167.
† Proc. Roy. Inst , xiv. p. 1.

insulation purposes, the convective transference of heat being stopped. If, however, the inner vessels were coated with a bright metallic deposit then the radiation influx is very greatly diminished   This is readily shown by making a half-silvered vessel   The radiation from the silvered and the clear sides respectively is compared by presenting each in turn to a thermopile connected to a galvanometer, whose indications are shown by a moving spot of light on the screen.   Two

Dry Air
Isolation

Vacuum
Isolation
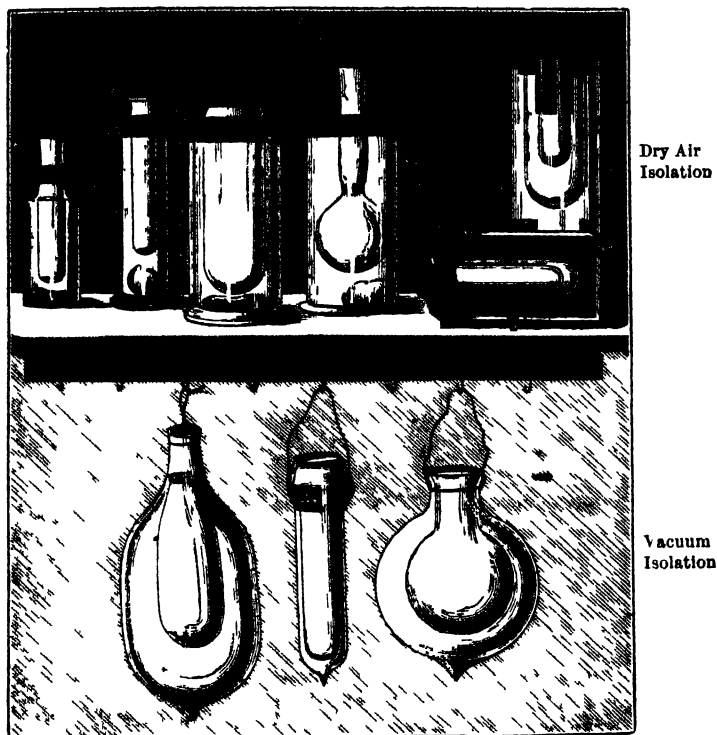
FIG 1

The upper vessels in this figure are for dry air isolation whereby the deposition of moisture at the low temperature was prevented   In each of these old forms it will be noted that a mass of phosphoric anhydride placed in the lower portion is required to absorb traces of water   The vacuum vessels described equally retard the loss as well as the gain of heat (as shown in Fig 3)

such vessels are filled with liquid air and hot water respectively ; scarcely any movement of the spot of light is seen when the silver side is turned to the pile, but on rotating to the unsilvered side a strong

deflection is observed, in one direction with the liquid air vessel and to the opposite side when the vessel of hot water is substituted.

Another aid to the heat insulation of vacuum vessels is the introduction of finely divided powders to the exhausted space : the results of the use of some of these are given in my discourse on " Liquid Air as an Analytic Agent."*
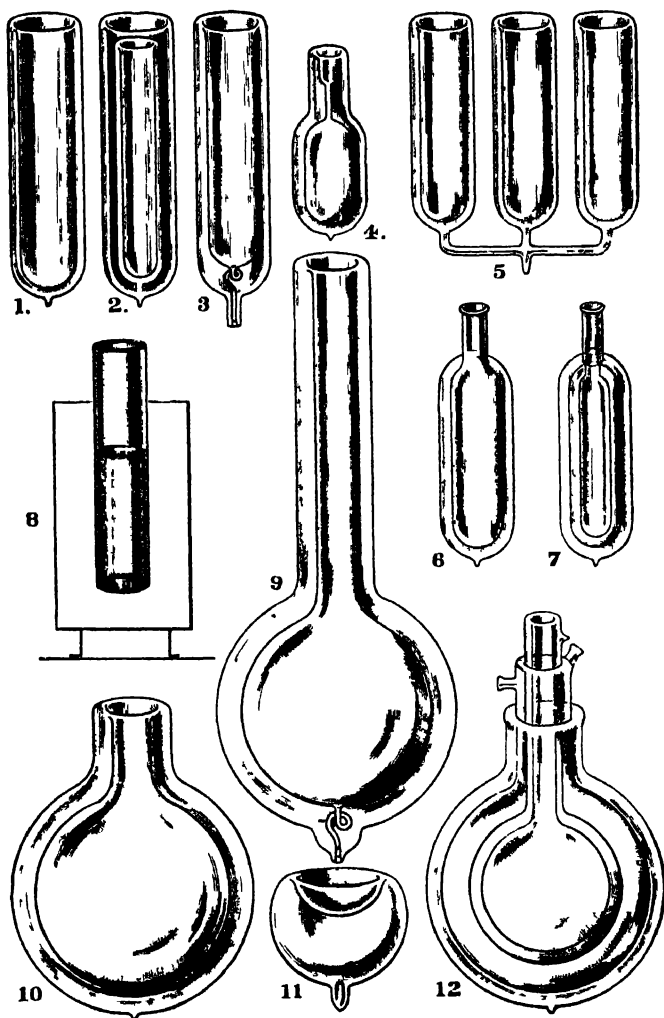
FIG 2

Another method of producing the requisite high vacua is by means of a mercurial vacuum made by distilling mercury through the annular space while exhausting by a good pump.* On placing a liquid gas in such a flask the mercury vapour left in the annular space is condensed as a bright mirror on the cool inner wall; and if used solely for low temperature work, this is entirely satisfactory, the need for silvering the inner surfaces is then partly obviated.

This action is illustrated in an exhausted globe containing a little mercury. There is a shallow depression in the globe into which a little liquid air is poured (see 11, Fig. 2); almost at once a mirror of mercury is deposited inside on the cooled part and the increased isolation results in a diminution of the rate of evaporation. A difficulty arises, however, if the vacuous space is not of reasonable cross-section, because the vapour of mercury is not only dense, but has a high viscosity, and therefore cannot get freely to the cooled surface, which results in the production of a poor mirror of limited extent. Thus, if another globe is taken having the mercury in a small bulb separated from the main globe by an inch of capillary tubing,† then on cooling a small area with a sponge of liquid air, the vapour saturating the globe is deposited as a localised mirror. If, however, a second area be then similarly cooled no deposit is obtained, because practically no mercury vapour can get in through the capillary; this is proved by decanting a little mercury out of the small bulb into the globe, when instantly a mirror is deposited on the cooled area.

The practical effect of this property is shown by the relative isolations of two cylindrical vacuum vessels in the same condition as to exhaust and both containing a little mercury in the bottom. The annular vacuum space in one is about 1 c.m. wide, while the width of the other is only about 2 mm. Liquid air is poured into both and the relative rates of evaporation measured by connecting successively to each, an indiarubber tube delivering into a gas jar filled and inverted over water. A metronome indicates the time taken to fill the jar with the evaporating air in each case; the result shows that the vessel with the narrow annular exhaust space is worse than the one with the wider space, and on examination this is explained by the smaller extension of the mercury mirror in the narrow-spaced vessel.

A pure water vapour discharge tube provided with two platinum wire electrodes illustrates the condensing action of liquid air in the production of a high vacuum in vacuum vessels for any vapours therein contained. The tube shown was about 5 c.m. diam. and 35 c.m. long. This tube is saturated with water vapour at the temperature of melting ice. On connecting the electrodes to a

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* Proc. Roy. Inst., xiv. p. 395.
† See Fig. 3, Proc. Roy. Inst., Jan. 12, 1894.

sparking coil the lilac-glow of hydrogen fills the tube. When a sponge of liquid air is applied in less than a minute the water vapour is condensed ; the glow disappears ; the tube passes through the phosphorescent stage, and finally becomes too highly vacuous for a discharge to pass. On removing the sponge the phenomena are reversed.

As concrete examples of the extent of the heat isolation, it can be stated that liquid air in 5-litre vacuum flask loses 12·5 grms per hour, or 8 per cent per day. If contents weigh 3650 grms., trace is left on the twelfth day. Heat exchange per minute per sq. c.m. = 0·007 calories.

Taking radiation law of heat exchange and silver emissivity, heat
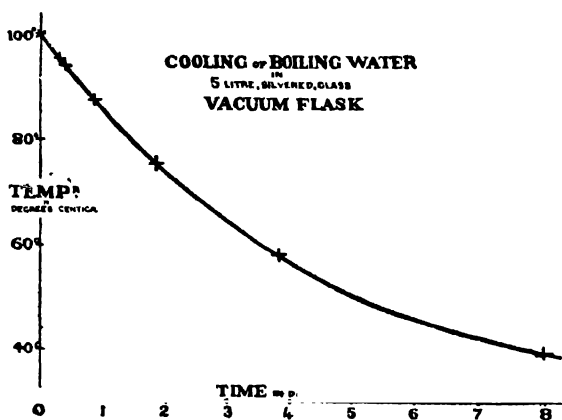
FIG. 3.

exchange by theory per min. per sq. c.m. = 0·015 calories, the observed experimental value being 0·01.

1·5 litre silvered vacuum vessel lost 9·5 grms. per hour, or 15 per cent on first day. Trace left on sixth day.

Fig. 3 gives the curve for decrement of temperature from the boiling-point of water in a silvered vacuum vessel, showing the same low rate of loss of heat as compared with gain of heat in the former example.

Some twelve years later a further advance was made by the application of the well-known absorptive power of charcoal. The possibility of the occlusion of gases in porous bodies has been a subject of scientific inquiry for more than two hundred years, and has been investigated by a long line of famous chemists. The Discourse on "New Low Temperature Phenomena," in the year 1905, was devoted to a consideration of the thermal evolution and absorption of gases by charcoal at low temperatures. A year later the application of this knowledge was made to the production of very

high vacua, by placing a small quantity of charcoal in a globular recess in the vacuous space of the flask. When such a vessel was filled with liquid air, the charcoal was also cooled and thus absorbed remaining traces of air, producing thereby a vessel with very high heat insulating qualities.

The employment of charcoal made it possible to use metals such as brass, copper, or nickel, instead of glass, for the construction of vacuum vessels, with obvious advantages. Metals give off small quantities of gas for a long time, which diminish the vacuum in such flasks, if it were not maintained by some charcoal, cooled to the low temperature of liquid air, or other liquefied gas, placed in the vessel. Many forms of such vessels have found a ready application to low temperature work, not only for storage and transport, but in cases where rough usage was unavoidable, or where the fractures to which
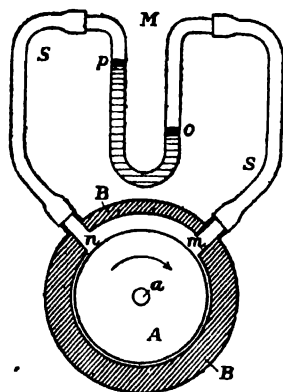
Fig. 4

glass is liable might be dangerous; also when high pressures are to be employed along with low temperatures metallic construction is necessary, and only by the addition of charcoal condensation can the necessary heat insulation be secured.

The most recent achievement in the attainment of a high exhaust is Dr. Gaede's invention of the Molecular pump, which is capable of producing a vacuum of ·000001 mm. of mercury.

The working principle of this pump is shown in Fig. 4. A is a revolving cylinder fixed on a shaft a enclosed in an outer casing B. In the inner side of B a groove n to m is cut, communicating at either end through the casing with a mercury gauge M. When the cylinder rotates from left to right, or clockwise, the friction set up amongst the molecules of the gas or air contained in the groove

causes it to be driven from *n* to *m*, and the mercury in the gauge rises to *p* in the left limb, owing to the diminished pressure, and is depressed to *o* in the right limb. The difference in pressure is proportional to the number of revolutions of the cylinder and the internal friction of the gas. In practice the grooves are cut in the cylinder, and the tongues, which project into the grooves, are fixed on the casing. The speed of rotation of the central shaft carrying the cylinder is about 8000 revolutions per minute.

The efficiency of this pump is seen when it is used direct on a large discharge tube 2 m. long and 6 c.m. in diameter, provided with electrodes in the manner of a De la Rue tube. In about a minute from starting at atmospheric pressure all stages of discharge at low pressures are traversed, and finally only a flickering phosphorescence is seen. A further test on liquid oxygen shows the manner in which a rapid evolution of gas is overcome. The melting pressure of oxygen is too low to be realised by usual exhaust methods, as was shown in the Discourse of January 20, 1911, when the solidification of oxygen was shown to be possible only by the exhaust produced by charcoal and liquid air. Formerly it was necessary to employ cooling by liquid hydrogen to obtain oxygen in the solid state. If, however, the fitting on the exhaust nozzle of the Gaede pump be directly connected to a vacuum vessel containing some 10 c.c. of liquid oxygen (isolated as usual by being surrounded with an outer vessel of liquid air), three minutes' working of the pump results in the oxygen being transformed into solid state.

Low Temperature Calorimetry.

The application of vacuum tube methods has resulted in bringing the law of Dulong and Petit into relation with the other laws governing the behaviour of the atoms. Working at ordinary laboratory temperatures Dulong and Petit had shown that the atomic heats for the various elements (got by multiplying the specific heat and atomic weight) was a constant of an approximate value six. For working at $50°$ Absolute ($-223°$ C.), a liquid hydrogen calorimeter has been constructed in which the specific heat of the various elements can be easily determined in terms of the volume of gas produced in cooling the substances. Under such conditions very different results from those previously obtained have been deduced. The atomic heats exhibit the same rough periodicity of function with atomic weights as is shown by other properties of the elements. A double curve demonstrates the complete parallelism between the atomic volumes and the atomic heats of the principal elements (see Fig. 7). In connection with speculations as to the constitution of the atoms, physicists had been putting different interpretations

on the structure of the atom, discussing voitices of electrons,
central positive charges, and so forth.   It was remarkable, in view of
these experiments, that some of them had predicted that the atomic
heats must be chiefly determined by the atomic volumes and the
elastic constants.

Atomic Specific Heats between the Boiling Points of Liquid Nitrogen and Hydrogen.

The Mean Atomic Specific Heats at 50° Absolute of the Elements, a Periodic Function of the Atomic Weights.

A method of determining the specific heat of substances at low
temperatures was described in a paper on " Studies with the Liquid
Hydrogen and Air Calorimeter,"* also in the abstract of a Friday
Evening Discourse in 1904 on " Liquid Hydrogen Calorimetry,"†
where the apparatus then used is illustrated.

Continuing the use of the same method, but with some modifica-
tion of the apparatus, the investigation has been extended to a large
number of inorganic and organic bodies.   In this later series of
experiments, the measurements of the specific heats of materials by
the liquid hydiogen calorimeter were made over a range of tempera-
ture from boiling nitrogen to boiling hydrogen, a fall of temperature
of some 57° Absolute.

Weighed pieces of the material are cooled to the temperature of
boiling nitrogen in a quartz cooling vessel of special design.   By a
simple mechanical device they are then released from this vessel, and
drop into liquid hydrogen in the calorimeter below.   The resulting
volumes of hydrogen evaporated are measured.   From this value and
a knowledge of the latent heat of the liquid hydrogen and the mass
of the substance, the specific heat can be calculated as follows :—

If V is volume of hydrogen at N.T.P. evaporated by the fall of
1 grm. of the substance through T degrees above the temperature of
boiling hydrogen, and s its specific heat, L being the volume of
hydrogen evaporated by 1 calorie, then

$$sT = \frac{V}{L}, \quad i.e. \quad s - \frac{V}{TL}.$$

The latent heat of liquid hydrogen is taken as 115 calories, and
therefore L = 97·05 c c. ; also in these experiments T is constant
(57°·5) therefore

$$s = V \times 0·0001792.$$

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* Roy. Soc. Proc., A, lxxvi. p. 325.
† Roy. Inst. Proc., xvii. p. 581.
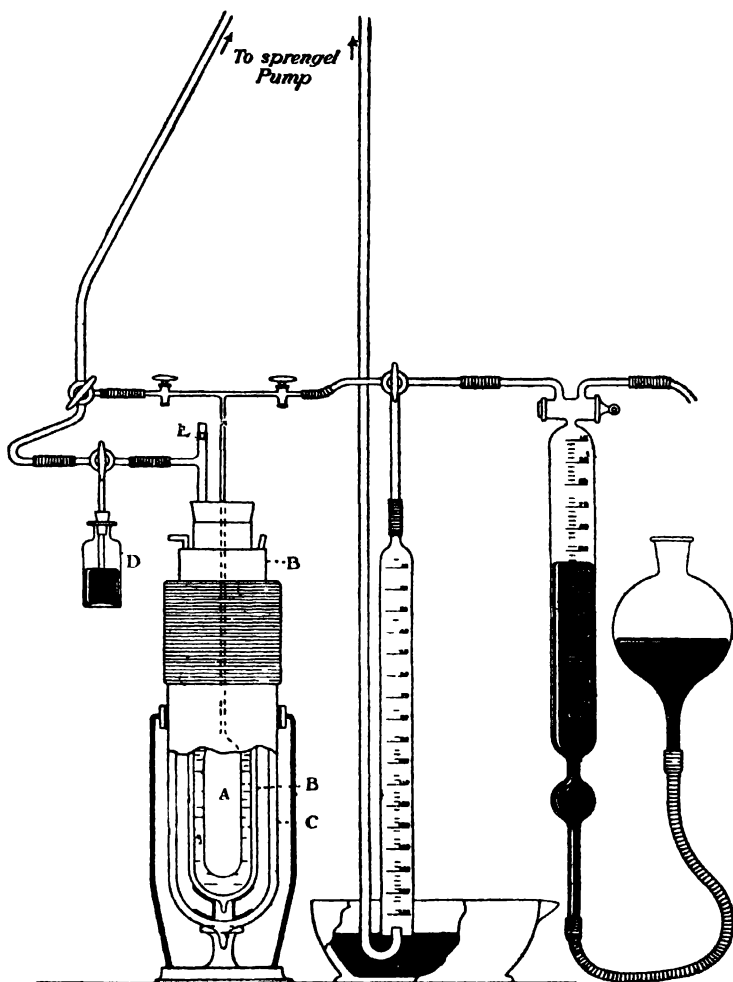
FIG. 5.

Thus the hydrogen volumes measured are reduced to V at N.T.P. and simply multiplied by the constant factor $0·0001792$, thereby giving the specific heat.

In an earlier Paper* the value of the latent heat of hydrogen was taken as $122·92$. Five observations were given varying $±5$ about this mean value. This was determined on the basis of $0·0291$ being accepted as the mean specific heat of lead from $15°$ C. to $20°$ Abs. Several Willard Gibbs vapour pressure formulæ, however, calculated from the vapour tensions of liquid hydrogen, give a mean value of 115 for the latent heat of hydrogen, so that the specific heat of lead over this range would seem to be $0·0272$.

In connection with the computation of the latent heat of liquefaction of hydrogen it is essential to know the value of the specific volumes of saturated hydrogen between $15°$ and $20°$ Abs. This was determined in the following simple manner : a carefully calibrated bulb A was charged with hydrogen to saturation at liquid hydrogen temperatures, and the volume of the hydrogen so required determined by pumping out the bulb. The figure (Fig. 5) shows the bulb A immersed in liquid hydrogen in vacuum vessel B, which is further isolated in the usual way in an external vacuum vessel C of exhausted liquid air. The hydrogen evaporating from the liquid was used to saturate the space to the same pressure as existed in B, the tube dipping into the bubbling bottle of hydrogen D was lengthened to more than barometer height when the liquid hydrogen pressure was reduced below atmospheric to obtain temperatures below the boiling point ; for this purpose the exhaust was connected by a stopcock on E. The various connecting stopcocks and collecting and measuring apparatus shown indicate the necessary manipulations.

The values obtained at the boiling point and near the melting point respectively are shown in the following Table :—

SPECIFIC VOLUME OF SATURATED HYDROGEN.

Temperature	Pressure	Vol. of Unit Weight (Specific Volume)	Ratio to Density of H at the same Pressure and 0° C
20·4 ' Abs.	760 mm.	747 4	14 94
15 3 ˥ ,,	115 ,,	3914	18·84

However, the relative weights of liquid and saturated vapour thus determined, only involve a correction of about 1% in the calculated latent heat, which is within the experimental variations.

Taking the value of 115 for the latent heat of hydrogen, the resulting value of the specific heat of lead from $80°$ Abs. to $20°$ Abs. is now $0·02399$. This is the mean value of a series of nearly

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* Roy. Soc. Proc., A, lxxvi., p. 325.

30 observations. The greatest variations from this mean value were 0·0247 and 0·0233, but the majority of the values varied to a much less extent. This is equivalent to an atomic specific heat of 4·965. It may be mentioned that a computation from Nernst and Lindemann's[*] real specific heats of lead within the same range of temperature gives the mean value 5 18.

In the observations with the liquid air calorimeter the specific heats were calculated in each case by direct comparison with lead observed at the same time, as explained in the earlier papers. This is most convenient because liquid air varies in composition on standing, and therefore in the volume evaporated by unit amount of heat.

Liquid Hydrogen Calorimeter.

The liquid hydrogen calorimeter is a glass cylindrical bulb vacuum vessel A (Fig. 6) of 50 c.c. capacity, silvered, with $\frac{1}{2}$ cm. slit. The inner diameter is 3 cm. On to the neck, contracted to about 1·7 cm., is sealed a glass tube B of equal diameter and 30 cm. long. This projects about 8 cm. through the brass coned fitting cap F of an ordinary slit silvered vacuum vessel in which it is supported. A side delivery tube, 1 cm. wide, provided with a stopcock D of 8 mm. bore, is sealed near the top of B. A short length of rubber tubing on the neck of F makes a gas-tight joint with B. To minimise splashing, and to reduce the impact of the falling pieces, a thin strip of german silver or lead E, bent out near the top into a shoulder about 1 cm. square, stands centrally in the calorimeter A. The strip is cut from a thin tube of about the same diameter as the calorimeter neck. A short length of the tube is left above the shoulder, and supports the strip by fitting loosely into the neck of A. The shoulder is arranged just above the level of the liquid hydrogen in A, which is at least three-quarters full. Some such device is essential in the use of this form of the liquid hydrogen calorimeter.

The calorimeter in its turn is immersed in liquid hydrogen in the supporting vacuum vessel C, the neck of the calorimeter being 8 to 10 cm. below the liquid hydrogen surface. This vacuum vessel C is only slightly wider than the lower part of A, and is provided with a coned cap F, whereby it is also supported and completely immersed in a wider vacuum vessel G containing exhausted liquid air. G is also fitted with a brass coned cover, fitting vacuum-tight to the cap F on C. Both caps are pierced by two thin tubes, one for fitting on to the filling syphons, the other, bent at right angles, serves for connecting to the exhaust in the case of the liquid air vessel, and in the case of the liquid hydrogen vessel to the stopcock leading the evaporating hydrogen through the upper part of the apparatus.

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[*] Sitzungsber. d. Berl. Akad., 1911, p. 494.
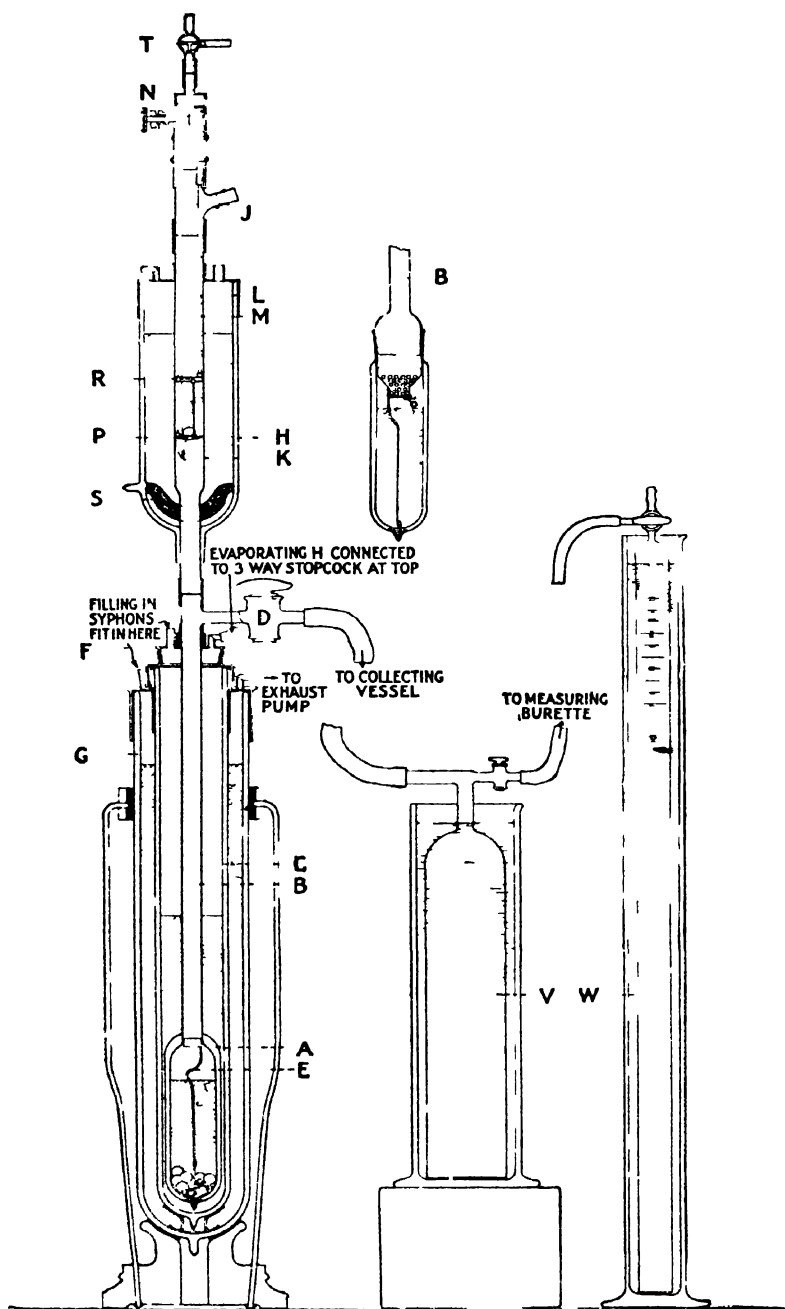
Fig 6

This arrangement thus charged only needs a little liquid air sucked in every one and a-half hours. The liquid hydrogen vessel will not need replenishing for at least four hours. The level of the liquid hydrogen in the calorimeter does not fall 1 cm. in six hours with constant use. The bulk of the materials added roughly compensates for the volume of the liquid hydrogen evaporated. It is important that this level should not materially change, since, after striking the shoulder, bodies move more slowly, are deflected on to the cold wall, and low results are obtained due to the longer cooling of the materials in the vapour before being immersed in the liquid hydrogen.

The isolation of the calorimeter was such that less than 10 c.c. of hydrogen gas evaporated from it per minute. The whole vacuum vessel combination is supported between cork-lined spring jaws mounted on a heavy metal base, on which the outer vacuum vessel rests.

The cooling vessel H is connected by india-rubber tube to the top of the calorimeter. It consists of an ordinary cylindrical slit silvered vacuum vessel, 30 cm. long and 7 cm. wide, with a central axial open tube K sealed in below. This tube passes through the liquid in the vacuum vessel. It has the same diameter below as the neck tube of the calorimeter. Near the top of the central tube a side tube J, of about the same diameter, and some 3 cm. long, serves for the introduction of the weighed pieces of material, which are all cooled previously to the temperature of liquid air, and then fall on to a thin metal pan P fitting loosely the tube K, where they remain about fifteen minutes. P is supported by being hinged to two thin ebonite rods, L and M, fixed to a brass fitting cemented on to the top. The rod L is not fixed directly to the disc but to a metal ring R. From the ring R two thin vertical steel wires are connected freely to two points on the circumference of the pan below. This rod and the attached ring can be given a vertical motion by a crank N in the top fitting, thereby tipping the pan and releasing the piece of material, which then falls freely down into the calorimeter. The level of the pan is approximately one-third the vertical height of the cooling vessel. Quartz was found to be safer than glass for the construction of this vessel. A high vacuum was maintained by filling with charcoal a cross-tube S, opening to the annular space.

At the temperature of boiling nitrogen, the convection currents in the central tube of such a vessel, when connected to the calorimeter below, have no serious effect on the temperature in the tube at a reasonable distance from the bottom, provided the central tube be not wide. The difference of temperature in the tube and in the surrounding liquid was found to be only $0 \cdot 5°$ when the tube was $1 \cdot 5$ cm. wide. With a larger pattern vessel the width of the central tube was increased to $2 \cdot 2$ cm., and even here the difference was under $3°$ at the level of the pan. These temperatures were measured by a small helium thermometer, consisting of a 4 c.c. bulb to which

was sealed a small mercury manometer of fine capillary tubing. The thermometer was filled with pure helium to 273 mm. pressure at 0° C. The reading of the mercury manometer thus gives, with slight corrections previously determined, the absolute temperature. It is scarcely necessary to add that, by exhausting the liquid nitrogen, a lower initial temperature than 78° Abs. can be secured.

The hydrogen evaporating from the liquid in the vacuum vessel C, in which the calorimeter is immersed, is employed in the interval of observations to maintain a hydrogen atmosphere through the neck of the calorimeter and the connected measuring tubes. Risk of solid air in the calorimeter neck is thus obviated. A simple arrangement of a three-way cock T, connected at the top of the brass fitting on the central tube of the cooling vessel, allows this to be manipulated. The hydrogen thus passes continually in at the tubular top of the fitting on the central tube of the cooling vessel, and out through the stopcock on the calorimeter neck, and through the cocks to the measuring vessels. When an observation is to be made, the three-way cock is turned to allow the hydrogen current to escape to the laboratory, thereby closing off the calorimeter, which now only connects to the collecting and measuring vessels V and W.

V consists of a glass tube 8 cm. in diameter and 40 cm. long, open at the bottom and provided with a wide T-piece at the top The tube is immersed to the neck in water in a glass cylinder, and is counterpoised by a weight and cord running over a pulley just above. It is thereby readily raised during the time gas is being evaporated from the calorimeter; this ensures that no back pressure is produced. One arm of the T-piece is open and connects to the stopcock D on the calorimeter neck; the other is provided with another small stopcock· and connects to a 200 c.c. gas burette W similarly immersed in water. This latter stopcock is closed during the collecting of the gas from a dropped piece of material. This being completed, the calorimeter stopcock is closed while the evaporated hydrogen gas is measured by transference to the burette, the slight continual evaporation from the calorimeter meanwhile finding a vent through the three-way cock T at the top of the cooling vessel, which is now turned on. These arrangements are necessary to secure the minimum impediment to the evaporating hydrogen, which is usually evolved in less than 10 seconds, any temporary back pressure being fatal to concordant results. At least 15 seconds are allowed for collecting the gas given off, and even longer, in some cases, with badly conducting bodies.

A slightly different form of calorimeter vacuum vessel was used on some occasions, but without modifying the results. Instead of the constriction at the top of A, a ground conical neck was used of the same diameter as the inner tube. This neck was fitted with a similar ground conical hollow tube sealed on to the tube B.

Anhydrous glycerin was used to make the ground joint tight at the low temperatures. The wider neck in some ways simplifies the preliminary manipulations, and allows a more efficient arrangement to be securely fixed for preventing splashing, and breaking the fall of the bodies dropped into the calorimeter. The arrangement is shown in the side sketch B (Fig. 6). It consists of a light counter-poised trap door hinged at the lower end of a conical brass or german silver tube, supported in and fitting to the inner tube of the calori-meter. A small lead ball on a wire soldered to the trap door keeps this closed until struck by a falling sphere, while shutting it again immediately after the sphere passes through. The conical tube above the trap door is pierced with several small holes to leave a free passage for the evaporating hydrogen. The addition of a gauze filter to inter-cept spray was found to be impracticable, the resistance introduced causing back pressure. In later work the calorimeters were con-structed of quartz, a little charcoal in the bottom of the annular space serving to maintain a very high vacuum isolation.

As far as possible the materials used were cast in the forms of spheres about .8 mm. diameter, and for this purpose the use of an ordinary bullet mould was found convenient. In the case of liquid bodies, the mould was first cooled by liquid air. Frequently liquids were frozen into solid cylinders in thin glass tubing, and pieces cut off after removing the glass mould. The metallic materials were in some cases fused into buttons of convenient weight in an exhausted quartz. tube. The lead, however, of which many pieces were re-quired, were cut from rod, and subsequently squeezed in a small spherical mould.

Volatile bodies were weighed at a low temperature on a light german silver pan supported by a thin platinum wire suspension from the balance pan about 2 cm. above the level of liquid air contained in a wide deep vacuum vessel. Some materials would not make coherent bullets or cast sticks. These were filled into very thin walled cylindrical metal capsules of equal weight, so that a preliminary determination of the volume of hydrogen evaporated by the metal of the capsule gave the correction. They were then cooled on an aluminium dish floating on liquid air, filled with the fluid, and weighed separately. Materials which could not be fused were com-pressed hydraulically into small blocks and cut up into pieces of suitable dimensions.

At least three pieces of every substance were dropped. The results rarely varied among themselves by more than 2 to 3 per cent. Very frequently the agreement was within 1 per cent. In order to ensure good results, uniformity of shape and size in the pieces of material used is desirable, so that the manner of release and fall shall be comparable : because in the use of this instrument the materials had to pass through a region of the neck, between the cooling vessel and the calorimeter, where a considerable gradient of

temperature exists. It was necessary that, as far as possible, the bodies used should be subjected to this variable region in the same manner, so that the amount of heat absorbed in transit should be nearly the same. This value was determined in the following manner. The warm portion of the calorimeter neck between the cooling vessel above and the vacuum vessels below was cooled by being surrounded with liquid air placed in a simple temporary fitting. Observations with various kinds of bodies were then made. The comparison of the reduced volumes now obtained with the values given by the ordinary use of this particular form of the instrument gives the correction factor. Many confirmations of the specific heats were made with this addition to the instrument. In the latest form of the calorimeter the neck is always surrounded with liquid nitrogen, thus abolishing all heat correction. This improved calorimeter gives results differing but slightly from the corrected values of the old instrument. The value of the atomic heat of lead is determined before and after any series of experiments as a check on the constancy of the instrument.

The values of the specific heats given will include any heat of transformation of glassy or crystalline modifications or other comparable change produced by the cooling to 20° Abs. Another effect is produced by some materials when used in the form of hydraulically compressed blocks. Such as are porous exhibit in varying degrees the phenomenon of heat evolution due to liquid hydrogen passing into the capillary spaces, thereby rendering the observed specific heat too great unless the proper correction is made. Any air occluded during the preliminary cooling of the porous material to liquid air temperature before being introduced to the hydrogen calorimeter is also included. Some of this air would be replaced by hydrogen through diffusion while in the hydrogen atmosphere in the central tube of the cooling vessel of boiling nitrogen ; but the true remedy is the preliminary cooling of such porous bodies in a hydrogen atmosphere at the temperature of liquid air. That heat evolution continued in many cases for some time after the dropping of the material was shown by an increased rate of evolution of hydrogen from the calorimeter. As stated above, this is normally less than 10 c.c. per minute. In some cases the introduction of porous material increased this for some time to more than 30 c.c. per minute.

The values set out in Table I for the mean atomic specific heats of 53 elements at about 50' Abs. represent the results of some 200 calorimetric observations. When plotted in terms of their atomic weights, they reveal definitely a periodic variation resembling generally the well-known Lothar Meyer atomic volume curve for the solid state. The relations between the two curves is shown in Fig. 7. If experiments were similarly made between the boiling points of hydrogen and helium then in all probability the atomic specific heats would be all very small and nearly constant.

Fig 7

Friday, February 13, 1914.

Sir James Crichton-Browne, J.P. M.D. LL.D. D.Sc. F.R.S.,
Treasurer and Vice-President, in the Chair.

Professor J. Norman Collie, Ph.D. LL.D. D.Sc. F.R.S.

The Production of Neon and Helium by the Electric Discharge.

The starting point of the following experiments by the author was
due to a number of observations on gases that are evolved when
many minerals are bombarded by the cathode rays in vacuum tubes.
Amongst the minerals experimented on, fluor spar was found to give
off a considerable amount of gas ; on the suggestion of Sir William
Ramsay this gas was examined for helium and neon, with the result
that a small amount of neon was found.   This observation led the
author to a long series of experiments, the interest of which lay in
the fact that helium often as well as neon made their appearance in
various tubes through which the electric discharge had been passed
in a high vacuum.

From the beginning, however, it had been always obvious that as
air contained both helium and neon great care must therefore be
taken, firstly, to entirely get rid of all the air in the experimental
tube by pumping it out·and subsequent washing out with some pure
gas, oxygen or hydrogen : secondly, to be sure that no air leaked
into the apparatus during the experiment.

About four months after the author had noticed the occurrence
of neon in the gases given off from fluor spar when bombarded by
the cathode rays, he heard that Mr. H. S. Patterson, who was working
at the University of Leeds, had obtained similar results ; since then
they had worked together, and later on Mr. Masson, of University
College, London, had joined in the research.   The idea of Mr.
Patterson that had led him to his experiments was that if it were
possible by means of the electric discharge to impart to hydrogen
atoms an extra electric charge, these hydrogen atoms might possibly
be converted into helium atoms.

In the joint work of the author with Mr. Patterson and Mr.
Masson a large number of different forms of apparatus were employed,
designed to test in every way conceivable what were the best con-
ditions for the production of the gases, and at the same time exclude
the possibility that the gases were occluded in the glass of the tubes

or in the metals used as electrodes. In one way many of the experiments were disappointing, for it was found that very often an experiment that had yielded the gases, when it was repeated gave none, but at the same time there were many positive experiments where it was almost impossible that the gases were due to any leak in the apparatus.

Some of the more important experiments were as follows : to prove that the gases were not occluded in the aluminium electrodes used, the aluminium was both fused in vacuo and the gases evolved tested ; aluminium was also dissolved and the hydrogen produced examined : in both cases neither helium nor neon could be detected. The glass used in making the experimental tubes was treated in the same way and negative results obtained. Glass bulbs were evacuated as far as possible by means of the mercury pump, and washed out with pure gases, and then heated for hours almost to their softening point, but no helium or neon leaked through from the outer air. Large quantities of mercury were boiled in vacuo, but not a trace of helium or neon was given off. In another experiment the tube was entirely jacketed by another tube that was so far evacuated as not to allow the electric spark to pass ; neon was found as usual in the inner tube, but what was remarkable, helium with only a small amount of neon was present in the gases in the outer tube. In another experiment a large glass bulb was surrounded by a coil of · wire and a powerful electrodeless discharge used : helium was found inside the bulb. Different metals were used as electrodes, copper, silver, platinum, iron, potassium, sodium, lithium, magnesium, uranium, etc., and in nearly every case helium, or helium and neon, proved to be present in the gases that were pumped off from the experimental tube. A quartz mercury lamp that had been in use over 3000 hours was found to contain a relatively large amount of helium and neon. A special form of lamp was therefore constructed consisting of an inverted U-tube made of quartz, the end dipping into mercury in two large test tubes, so arranged that the level of the mercury at the top of the U-tube could be raised and lowered. A side tube from the top of the apparatus led to a pump so that the gases could be pumped out and examined. This lamp was running for over two months, and gave helium mixed with a small quantity of neon during the whole period. For the first few weeks the top of the U-tube was surrounded by the air, but for the rest of the time it was enclosed in a jacket filled with water ; the reason for doing this was that quartz is known to be pervious to helium and neon at high temperatures, i.e. 1000 C.

The summary of all these experiments had been : helium and neon did not come from the glass of the apparatus ; the electrodes could not be made to give either of these gases by heating or by dissolution, and as far as possible all leak of air into the apparatus was excluded, yet in a very large number of experiments both helium

and neon appeared in the tubes after a powerful electric discharge had been passed for some hours.

In December 1918, Professor Strutt, in a note to the Royal Society, stated that he had repeated the experiments of the authors, and had failed to confirm them. He suggested that pumping out the gases and transference to another apparatus for the purpose of testing for helium and neon, would favour leakage of small quantities of air, quite sufficient to account for the helium and neon obtained by the authors. He had therefore used a form of apparatus in which all the operations could be carried out without any such transference. To account for Professor Strutt's failure to obtain positive results was difficult, for, as had been already pointed out, the authors found great difficulty often in repeating any particular experiment ; moreover, in several of the positive experiments apparently helium but no neon appeared in the experimental tube.

This fact cannot be explained by air leakage, for air contains four or five times as much neon as helium. At present the investigation was only begun ; many more experiments would have to be made, for the source of the helium and neon was still obscure ; but if it could be proved that these gases were produced from many metals and other substances under the influence of the cathode discharge, it it obvious that it would be a discovery of the most far-reaching importance
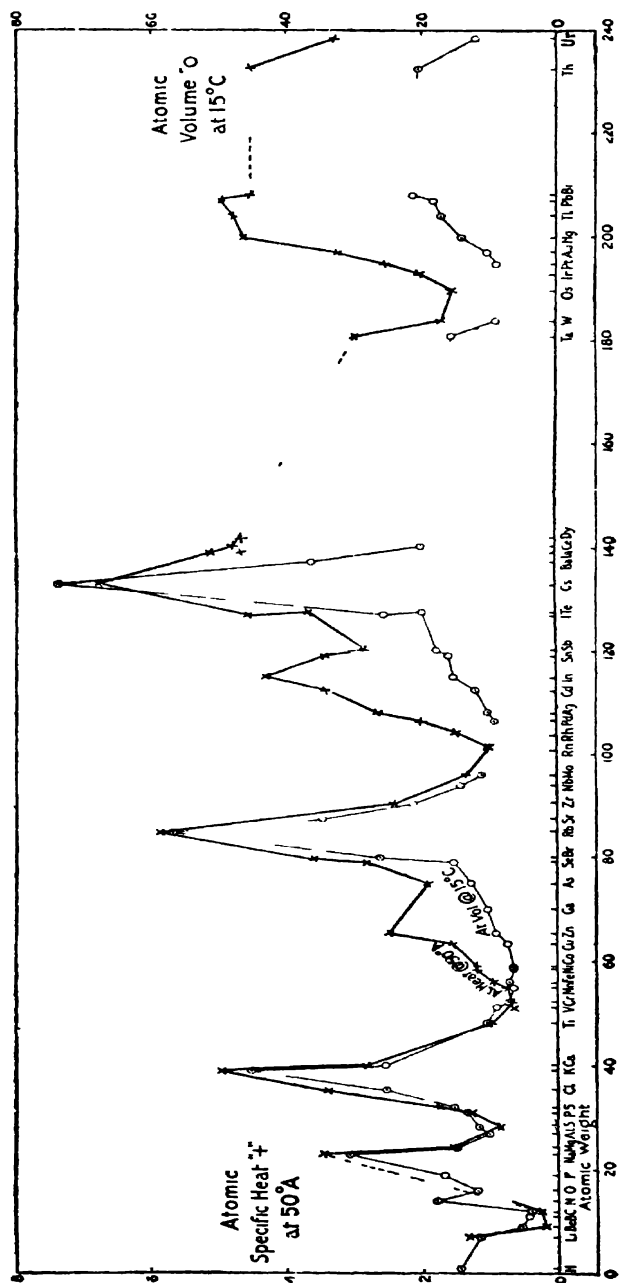
[J. N. C.]

Friday, February 27, 1914.

SIR JAMES CRICHTON-BROWNE, J.P. M.D. LL.D. F.R.S.,
Treasurer and Vice-President, in the Chair.

PROFESSOR W. A. BONE, D.Sc. Ph.D. F.R.S.

Surface Combustion.

DURING his researches upon Flame,* Sir Humphry Davy discovered,
in 1817, that the constituents of a combustible mixture will com-
bine slowly below the ignition temperature ; this led him to enquire
whether, seeing that the temperatures of flames far exceed those at
which solids become incandescent, a metallic wire can be maintained
at incandescence by the combination of gases at its surface, without
actual flame. He thereupon tried the effect of introducing a warm
platinum wire into a jar containing a mixture of coal-gas and air
rendered non-explosive by an excess of the combustible constituents ;
the wire immediately became red hot, and continued so until nearly
the whole of the oxygen had disappeared.

We will repeat the experiment, in a modified form, with the aid
of a platinum crucible and a Bunsen burner. If the platinum
crucible be warmed by the flame, and the flow of the explosive
mixture through the burner be momentarily arrested, and then
immediately renewed, the gases, instead of burning with flame at the
burner head, will immediately combine without flame over the
platinum surface, causing it to glow.

During the twenty years which followed Davy's discovery, several
distinguished chemists (William Henry and Thomas Graham in this
country, but more particularly Dulong and Thénard, and independ-
ently Dobereiner in France) experimented upon the slow combination
of gases at temperatures below the ignition point, in contact with hot
solids, whereby it was established (1) that hot solids, and pre-
eminently metals of the platinum group, have the power of inducing
gaseous combustion at relatively low temperatures ; and (2) that
hydrogen is of all combustible gases, the most susceptible to this
action.

The mechanism of this induced slow surface combustion formed
the subject of a celebrated controversy between Faraday and De la
Rive in 1834-5. De la Rive held the view that it consists essentially
in a series of rapidly alternating oxidations and reductions of the

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* Collected Works, vol. vi. p. 8.

surface ; Faraday, on the other hand, contended that the function of the surface is to condense both the oxygen and the combustible gas, thus producing in the surface layers a condition comparable to that of high pressure. But, owing to lack of crucial experiments, no satisfactory theory of the phenomenon could be evolved, nor, with the exception of the famous " Döbereiner Lamp," was there any practical outcome of this early work. In 1836 interest in the subject suddenly dropped, and was not revived for half a century.

Meanwhile, the researches of Deville upon the dissociation of steam and carbon-dioxide at high temperatures led to the notion, which was strongly upheld by the late Frederick Siemens, that inasmuch as incandescent surfaces promote dissociation, they must necessarily hinder combustion. This, of course, is fallacious ; we now recognize that if, as Deville proved, an incandescent surface accelerates the dissociation of steam, it must, according to a principle enunciated by Ostwald, of necessity accelerate the combination of oxygen and hydrogen in like degree, provided always that the surface remains chemically unaltered.

A notable demonstration of the possibility of realizing flameless incandescent surface combustion in contact with metals other than those of the platinum group was given by Thomas Fletcher in a lecture at the Manchester Technical School as far back as 1887.[*] He injected a mixture of gas and air on to a large ball of iron wire, flame being used at first in order to heat the wire to the temperature necessary to induce a continuous surface combustion ; on extinguishing the flame, by momentarily stopping the gaseous mixture, the combustion continued without any flame, but with an enormous increase of temperature. Fletcher grasped three important points, namely : (1) that " this invisible flameless combustion is only possible under certain conditions," (2) " that the combustible mixture shall come into absolute contact with a substance at high temperature. . . ," and (3) that " in the absence of a solid substance at a high temperature, it is impossible to cause combustion without flame " ; but, so far as I am aware, he did not follow up the matter beyond this point, either in its theoretical aspects or practical applications, and his work had but little influence upon contemporary opinion or practice.

My own investigations upon surface combustion began in 1902 with a systematic attempt to elucidate the factors operative in the slow combination of hydrogen and of carbon monoxide in contact with various hot surfaces (e.g. porcelain, fire-clay, magnesia, platinum, gold, silver, copper and nickel oxides, etc.) at temperatures below 500°.[*] Into the details of these earlier experiments, which preceded and led up to the technical developments about which I shall speak later, 1 do not propose to enter ; it will be sufficient for my present purpose if I say that it was proved beyond all question

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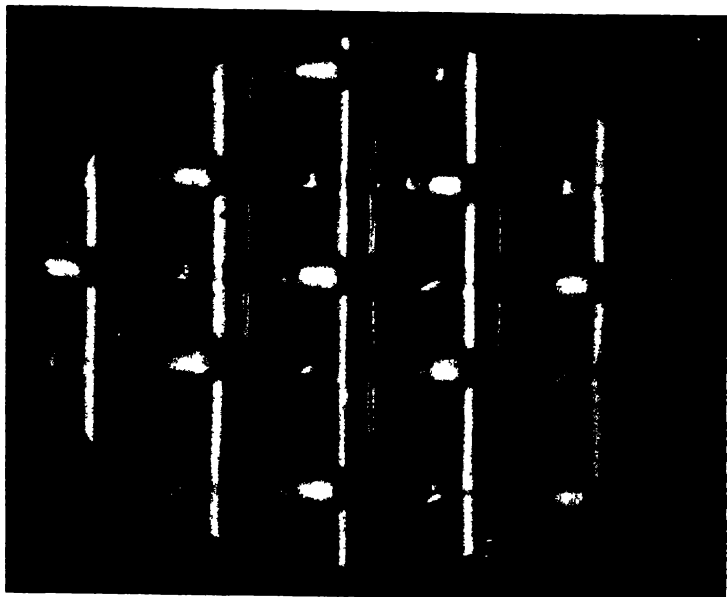
Fig. 1.

Fig 2.

(1) that the power of accelerating gaseous combustion is possessed by *all* surfaces at temperatures below the ignition point in varying degrees, dependent upon their chemical characters and physical texture ; (2) that such an accelerated surface combustion is dependent upon an absorption of the combustible gas, and probably also of the oxygen, by the surface, whereby it becomes "activated" (probably ionized) by association with the surface ; and (3) that the surface itself becomes electrically charged during the process.   Finally, certain important differences between homogeneous combustion in ordinary flames and heterogeneous combustion in contact with a hot surface from a chemical point of view were established, so that there can be no longer any doubt as to the reality of the phenomenon.*

The fact that such catalytic combustion depends upon an intimate association of the surface with the combining gases is beautifully illustrated by two photomicrographs of the surface of a silver gauze taken *before* and *after* a long series of experiments in which it was employed as the catalysing medium for the combination of hydrogen and oxygen at 400 C. (848° F.).   Fig. 1 shows the original smooth condition of the surface, and Fig. 2 shows the "frosted" effect produced by the deep "pitting" action of the reacting gases during their absorption and "activation" by the surface.

My next contention is that if hot surfaces possess the power of accelerating gaseous combustion at temperatures below, or in the neighbourhood of, the ignition point, the same power must also be manifested in even a greater degree at higher temperatures, and especially so when the surface itself becomes incandescent.   Indeed, there are experimental grounds for the belief that not only does the accelerating influence of the surface rapidly increase with the temperature, but also that the differences between the catalysing powers of various surfaces, which at low temperatures are often considerable, diminish with ascending temperatures until at bright incandescence they practically disappear.

Such considerations as I have thus briefly explained convinced me some years ago that if an explosive gaseous mixture be either injected on to or forced through the interstices of a porous refractory incandescent solid under certain conditions, which will be hereafter explained, a greatly accelerated combustion would take place within the interstices or pores, or, in other words, within the boundary layers between the gaseous and solid phases wherever these may be in contact— and the heat developed by this intensified combustion would maintain the surface in a state of incandescence *without any development of flame*, thus realizing the conception of *flameless incandescent*

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* Bone and Wheeler, *Phil. Trans. Roy. Soc*, 1906 (A. 206, pp. 1–67), also further (unpublished) results (1905–12) in collaboration with Messrs. G. W. Andrew, A. Forshaw, and H. Hartley, which are summarized in *Berichte der Deutschen Chem. Ges.*, 1913.

surface combustion, as a means of greatly increasing the general efficiency of heating operations wherever it can be conveniently applied.

There are critics who, whilst admitting the accelerating influence of an incandescent surface upon gaseous combustion, are sceptical about the process being really flameless. The force of such objections largely disappear when we get into close quarters with the phenomenon, and realize how extremely slow a transaction flame combustion really is when considered in terms of molecular time. Take, for example, the case of such a quick-burning mixture as electrolytic gas $(2H_2 + O_2)$. When this is ignited at atmospheric pressure, the flame is initially propagated by conduction with a uniform slow velocity of 20 metres per second, and during this initial period of "*inflammation,*" the total duration of chemical change in each successive layer is something like the order of $\frac{1}{50}$ second, an interval of at least one hundred million times as long as the average interval between successive molecular collisions in the gas. Even after "*detonation*" has been set up in the mixture, when the combustion is propagated from layer to layer as a wave of adiabatic compression, at a velocity of 2820 metres per second, the total duration of chemical change is still of the order of $\frac{1}{5000}$ or $\frac{1}{10000}$ second, or about a million times as long as the interval between successive molecular collisions.

To illustrate how a flame may be extinguished by the introduction of an active catalysing surface, I will perform an experiment which was first exhibited here a year ago by my colleague Professor the Hon. R. J. Strutt, who has very kindly lent me his apparatus. Most of you will be familiar with his discovery of the active modification of nitrogen produced by a powerful electric discharge. This bulb (capacity 300 c.c.) is full of rarefied nitrogen, at a pressure of about $\frac{1}{10}$ mm. ; and in the side tube lies an oxidized copper wire, which fits it as closely as is consistent with easy sliding.

If the nitrogen in the bulb be subjected to a powerful electrodeless discharge, it is transformed into an active condition; the gas continues to glow brilliantly, owing to the fact that the "active" modification is reverting to the ordinary kind producing a luminosity which may be regarded as a condition analogous with flame. The glow will last for a minute or more during the progress of the chemical reversion, and finally dies out when the latter is completed

But if, on repeating the experiment, the bulb be tilted so that the oxidized copper wire drops into the glowing gas, the luminosity is instantly extinguished. This shows that the reversion process is so enormously accelerated by the surface that practically the whole of the chemical action is concentrated at the surface, and instantaneously completed there, thus extinguishing the glow.

I think we have, in Professor Strutt's experiment, a close analogy

to what I conceive as occurring when an incandescent surface is employed to accelerate ordinary gaseous combustion ; the action is so concentrated at the surface that a substantially "flameless" effect results. I want to emphasize the fact that the incandescent solid plays a specific rôle in this surface combustion ; it is no mere idle looker-on at the surging crowd of reacting molecules which swarm around it. On the contrary, it so galvanizes and incites the dormant affinities between the combustible gas and oxygen, that the stately minuet of ordinary combustion gives place to the wild intoxication of the Venusberg.

The manner in which the surface acts is still perhaps a matter of conjecture, but the fact that it so acts can no longer be disputed. In a discussion which took place at the British Association in 1910, Sir J. J. Thomson insisted that combustion is concerned not only with atoms and molecules, but also with electrons, *i.e.* bodies of much smaller dimensions and moving with very high velocities, and suggested that in reference to the influence of hot surfaces in promoting combustion it was not improbable that the emission of charged particles from the surface was a factor of primary importance. It is known that incandescent surfaces emit enormous streams of electrons travelling with high velocities, and the actions of these surfaces in promoting combustion may ultimately be found to depend on the fact that they bring about the formation of layers of electrified gas in which chemical changes proceed with extraordinarily high velocity.

The New Processes of Incandescent Surface Combustion.

Leaving the theoretical aspects of the subject, I will now describe some of the more important features of two processes of incandescent surface combustion evolved at the works of Messrs. Wilsons and Mathiesons, Ltd., in Leeds under my direction, with the assistance of Mr. C. D. McCourt, in which a homogeneous explosive mixture of gas and air, in the proper proportions for complete combustion (or with air in slight excess thereof), is caused to burn without flame in contact with a granular incandescent solid, whereby a large proportion of the potential energy of the gas is immediately converted into radiant form. The advantages claimed for the new system, now known as the "Bonecourt" system, are : (1) the combustion is greatly accelerated by the incandescent surface, and, if so desired, may be concentrated just where the heat is required ; (2) the combustion is perfect with a minimum excess of air ; (3) the attainment of very high temperatures is possible without the aid of elaborate regenerative devices ; and (4) owing to the large amount of radiant energy developed, transmission of heat from the seat of combustion to the object to be heated is very rapid. These advantages are

so uniquely combined in the new system that the resultant heating effect is, for many important purposes not only pre-eminently economical, but also easy of control.

Diaphragm Heating and its Applications.

In the first process the homogeneous mixture of gas and air is allowed to flow under slight pressure through a porous diaphragm of refractory material from a suitable feeding chamber (see Fig. 3),
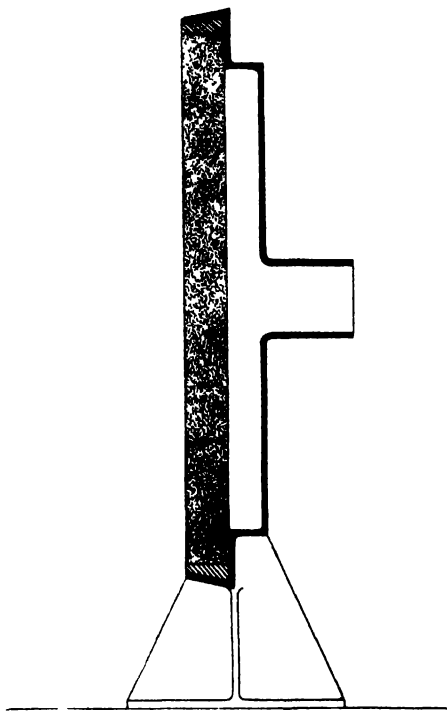
FIG. 3.—DIAPHRAGM, SECTIONAL VIEW.

and is caused to burn without flame at the surface of exit, which is thereby maintained in a state of red-hot incandescence. The diaphragm is composed of granules of firebrick, or other material, bound together into a coherent block by suitable means; the porosity of the diaphragm is graded to suit the particular kind of gas for which it is to be used. The diaphragm is mounted in a suitable casing, the space enclosed between the back of the casing

and the diaphragm constituting a convenient feeding-chamber for the gaseous mixture. Such a mixture may be obtained in either of two ways, namely (1) by means of suitable connections through a Y-piece with separate supplies of low pressure gas and air (2 or 3 inches W.G. is sufficient), or (2) by means of an "injector" arrangement connected with a supply of gas at a pressure of 1 to 2 lb. per sq. inch ; the gas in this case draws in its own air from the atmosphere in sufficient quantity for complete combustion, the proportions of gas and air being easily regulated by a simple device.

We will now start up a diaphragm. Gas is first of all turned on and ignited as it issues at the surface ; air is then gradually added until a fully aerated mixture is obtained. The flame soon becomes non-luminous, and diminishes in size ; a moment later, it retreats on to the surface of the diaphragm, which at once assumes a bluish appearance ; soon, however, the granules at the surface attain an incipient red heat, producing a curious mottled effect ; finally, the whole of the surface layer of granules becomes red-hot, and an accelerated "surface combustion" comes into play. All signs of flame disappear, and there remains an intensely glowing surface throwing out a genial radiant heat which can be steadily maintained for as long as required.

Whilst the diaphragm is in operation before you, I may point out some of the more striking features of the phenomenon which it presents. *Firstly*, the actual combustion is confined within a very thin layer—$\frac{1}{8}$ to $\frac{1}{4}$ inch only—immediately below the surface, and no heat is developed in any other part of the apparatus. Kindly observe that whilst the front of the diaphragm is intensely hot, the back of the apparatus is so cold that I can lay my hand on it. *Secondly*, the combustion of the gas, although confined within such narrow limits, is perfect, for when once the relative proportions of gas and air have been properly adjusted, no trace of unburnt gas escapes from the surface. *Thirdly*, the temperature at the surface of the diaphragm can be instantly varied at will by merely altering the rate of feeding of the gaseous mixture ; there is practically no lag in the temperature response, a circumstance of great importance in operations where a fine regulation of heat is required. *Fourthly*, a plane diaphragm such as this may be used in any position, i.e. at any desired angle between the horizontal and vertical planes. *Fifthly*, the diaphragm method is amenable to a variety of combustible gases —coal or coke oven gas (either undiluted or admixed with water gas), natural gas, petrol-air gas, carburreted water gas are all well suited in cases where unimpeded radiation is required. *Finally*, the incandescence in no way depends upon the external atmosphere. When once the diaphragm has become incandescent, and the proportions of air and gas supplied in the mixing chamber at the back have been properly adjusted, the surface will maintain its incandescence unimpaired, even in an atmosphere of carbon dioxide.

I need hardly point out to you the many obvious purposes, domestic and industrial, to which "diaphragm heating" may be applied. In the domestic line, the boiling of water, grilling, roasting and toasting are at once suggested, and although the best existing types of gas fires are thoroughly hygienic and efficient, I think that the diaphragm may come in for the heating of apartments; at any rate experiments are being carried out in that direction.

I have recently been told of a large restaurant in London where they are grilling by means of an electric radiator fixed horizontally above the work so that the radiant energy is directed downwards on to it. It has been claimed that the value of the recovered fat, which in the ordinary method of grilling drops into the fire and is consumed,
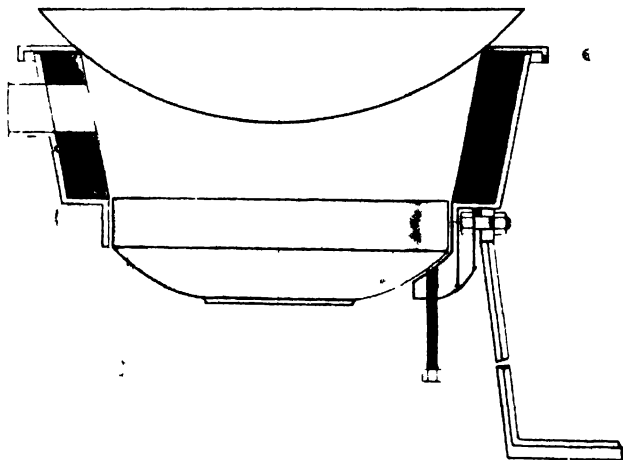
FIG. 4 —DIAPHRAGM FOR BOILING SUGAR SOLUTIONS, ETC

has more than paid for the electricity used. With a diaphragm, similar advantages can be secured with gas at a considerably less cost; for comparing gas of net calorific value 500 B.Th.Us. per cub. ft. at 2s. 6d. per 1000 cub. ft. with electricity at 3d. per unit, the initial cost of a given amount of energy is about 14 times greater in the form of electricity than in the form of gas.

Turning now to the industrial field, I had the satisfaction of visiting not long ago a large confectionery factory where the diaphragms have been employed for more than a year for the boiling and concentrating sugar solutions. The solution is boiled in a copper pan over a 13-in. diameter circular diaphragm (see Fig. 4); the

supply of gaseous mixture is controlled by one lever which operates in a single movement the gas and air cocks. The ignition is effected automatically by means of a small pilot light. Each boiler does 10 to 12 heats per diem, each lasting twenty minutes, and some of the diaphragms have been in continuous daily use for about a year. I saw in the factory a battery of thirteen such boiling pans, all in constant use, and was informed that the gas consumption was not more than half what it formerly used to be when the pans were heated over ordinary atmospheric flame burners. The secret of this higher efficiency lies in the fact that gas flames are a very unsatisfactory means for boiling liquids in metallic vessels, owing to the non-conducting layer of relatively cool gas which forms between the flame and the undersurface of the pan ; but with a diaphragm the large percentage of radiant heat is quickly absorbed by the vessel and transferred to the liquid with high efficiency.

Moreover, in evaporating liquids it is possible to use an overhead diaphragm, directing the radiation downward on to the surface of the liquid, thus eliminating altogether the influence of the containing vessel. In this way only the upper layers of the liquid are actually heated up to the working temperature, whilst the evaporation is extraordinarily rapid and efficient. Given a sufficiently cheap high-grade gas there would appear to be endless possibilities for diaphragm heating in the industrial field.

Incandescent Surface Combustion in a Bed of Refractory Granular Material.

The second process is applicable to all kinds of gaseous or vaporized fuels ; it consists essentially in injecting, through a suitable orifice at a speed greater than the velocity of back-firing, an explosive mixture of gas (or vapour) and air in their combining proportions into a bed of incandescent granular refractory material which is disposed around or in proximity to the body to be heated.

I can perhaps best describe the process by the aid of two diagrams showing its applications to the heating of crucible and muffle furnaces. Fig. 5 shows the process as applied to a crucible furnace. The crucible is surrounded by a bed of refractory incandescent granular material. The mixture of gas and air is injected at a high velocity through a narrow orifice in the base of the furnace, and as it impinges upon the incandescent bed, combustion is instantaneously completed without flame.

The seat of this active surface combustion is in the lowest part of the bed ; the burnt gases, rising through the upper layers, rapidly impart their heat to the bed, maintaining it in a high degree of incandescence. Fig. 6 shows a similar arrangement for the heating of a muffle furnace which needs no further explanation.

It is obvious that this process is capable of adaptation to all kinds of furnace operations, as, for example, to the heating of crucibles, muffles, retorts, and to annealing and forging furnaces generally. Moreover, it is not essential that the bed of refractory material should be very deep ; indeed a quite shallow bed suffices to complete the combustion. Neither is it necessary that the bed shall be disposed *around* the vessel or chamber to be heated ; for if contact with the burnt products is not objectionable, a shallow bed may be arranged
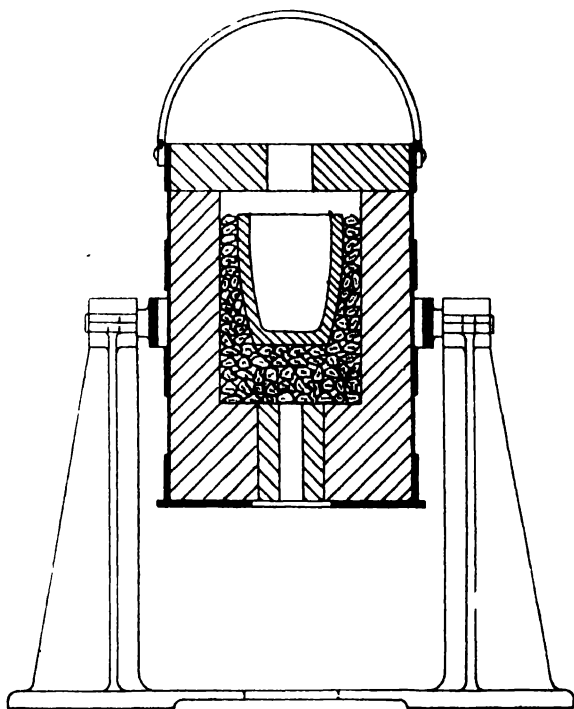
Fig. 5.

within the heating chamber itself (Fig. 7) : or the refractory material may be equally well packed into tubes, or the like, traversing the substance or medium to be heated. The last-named modification is, as we shall see later, specially important in relation to steam-raising ˙in multitubular boilers.

By means of this process much higher temperatures are attainable with a given gas than by the ordinary methods of flame combustion without a regenerative system, and, as a matter of fact, we have found

that with any gas of high calorific intensity (such as coal gas, water gas, or natural gas) the upper practicable temperature limit is determined rather by the refractoriness of the material composing the chamber to be heated (i.e. the muffle or crucible) than by the possibilities of the actual combustion itself. When I tell you that in a crucible fired by coal gas on this system we have melted Seger-cone No. 39, which according to the latest determination of the German Reichsanstahlt melts at 1880° C. (3416° F.), and also that we can
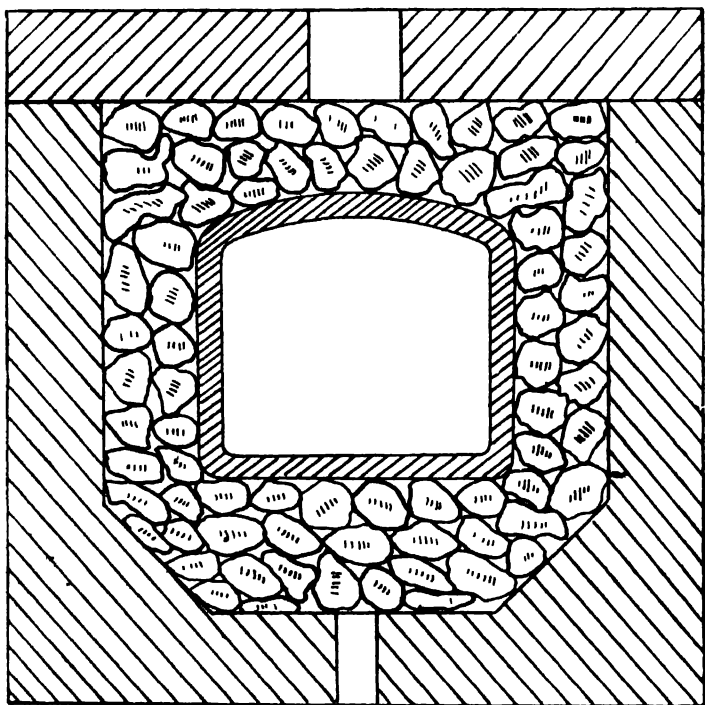
FIG. 6.

easily melt platinum, you will appreciate the possibilities of the method in regard to high temperatures with gas-fired furnaces.

The maximum temperature obtainable, without "regenerative" appliances, with any particular gas will obviously depend upon the relative heat capacities of their products of combustion for a given heat development in the bed. In this connection, it is of interest to compare the principal gaseous fuels available for industrial operations in the order of their calorific intensities, as follows :—

THE COMBUSTION OF TYPICAL GASEOUS FUELS.

	Per Cubic Foot of Gas Burnt			Per 100 B.Th.U's *net* developed on Combustion			
	Net B.Th.U's	Vol. of Air Required	Vol. of Products	Vol. of Air Required	Vol. of Combining Mixtures	Vol. of Products	Relative Heat Capacities of Products
Blue Water Gas... ...	290	2·290	2·82	0·79	1·14	0·97	0·95
Coal or Coke Oven Gas	500	4·656	5·36	0·93	1·13	1·08	1·00
Producer Gas	140	1·166	2·00	0·84	1·50	1·43	1 38
Blast Furnace Gas ...	100	0·716	1·58	0·72	1·72	1·58	1·52

Now, whilst with coal gas, coke oven gas or water gas, it should be easily possible, without regeneration, to obtain in a refractory granular bed temperatures of up to at least 2000° C. (or say 3630° F.), with a low-grade producer gas, such as Mond gas, about 1500° C. (or say 2730' F.), would probably be the approximate maximum without regeneration. But with some degree of heat recuperation, which in large furnaces is quite practicable, still higher temperatures would be attainable.

Moreover, within the maximum limits, the heating with any kind of gas is very uniform, economical, and controllable; indeed the temperature for a given furnace fired by gas of uniform composition is chiefly controlled by the amount of gas burnt, or in other words, the rate of heat development in the bed. And as for economy, tests made about three years ago in Leeds under my supervision upon medium-sized muffle furnaces convinced me that to maintain a given temperature between say 800 and 1400° C., a properly constructed "surface combustion furnace" would require between 70 and 40 per cent only of the gas used in an ordinary flame-heated furnace of the same dimensions, and that the advantage in favour of "surface combustion" would increase rapidly with the working temperature.

This was confirmed by independent competitive trials carried out in New York shortly after my lectures there in the autumn of 1911, in which our surface combustion furnaces were pitted against the best American types; it was proved that in order to maintain a temperature of 1400° C. we practically halved their gas consumption, whilst to maintain 800° C. our consumption was about 0·7 of theirs.

Anyone who understands furnace design and construction will appreciate the many difficulties which are necessarily encountered in applying a new and revolutionary idea of this sort to the firing of
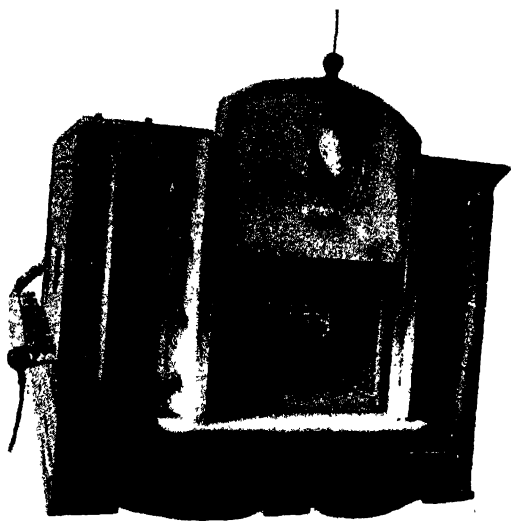
Fig. 7.
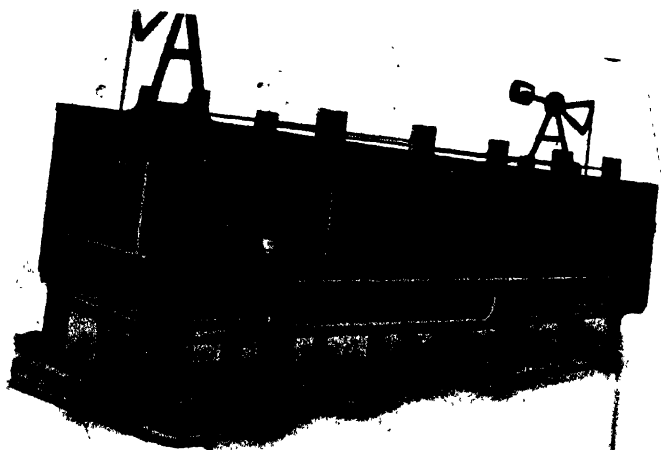
Fig. 8.

large industrial furnaces. Indeed, the new conditions of heating are so radically different from the old, that a new experience has to be built up. There are problems connected with the proper feeding and distribution of gaseous mixture, with the dimensions and arrangement of the combustion beds, and with the refractiveness of the furnace walls, which have to be solved. Nevertheless, judging from reports that reach me from time to time, substantial progress has been made in the direction of gas-fired crucible furnaces for brass and aluminium melting, annealing furnaces, and forging furnaces, the latter fired with producer gas with regeneration of gas and air. Some large annealing furnaces (for example, Fig. 8) are now running satisfactorily in industrial establishments on both Mond gas and town gas, and I understand that brass melting can be carried out in 50 to 60 lb. charges in tilting crucible furnaces with the remarkably low consumption of about 1·75 cub. ft. per pound of metal melted and poured.

Surface Combustion as Applied to Steam Raising.

I now come to an important application of the new process to the raising of steam in multitubular boilers ; not that the application of surface combustion is limited to boilers of the multitubular type, but because our investigations have so far been principally made with these.

It is well known that the gas-firing of steam boilers has not been very successful from the point of view either of thermal efficiency or of rate of evaporation. In this country the gases available for steam-raising purposes on a large scale are principally (1) blast furnace gas, of which there are large surpluses available in all iron-smelting areas ; (2) the surplus gas obtainable during the manufacture of coke in by-product ovens ; and (3) producer gas of various compositions, but more particularly that manufactured under ammonia recovery conditions. In the United States, and some other oil-producing countries, natural gas of high calorific power is also available. All these gases have been found to be amenable to the system I am about to describe.

It has been estimated by a prominent British blast furnace engineer that the thermal efficiency of the best type of water-tube boiler, fired by blast furnace gas, does not exceed about 55 per cent., whilst in the case of boilers fired by coke oven gas the average thermal efficiency probably does not much exceed 65 to 70 per cent. But on applying the principle of surface combustion to the gas-firing of multitubular boilers we have been able to obtain results with coal gas corresponding to the transmission of nearly 95 per cent of the *net* calorific value of the gas to the water in the boiler.

Our first experiments in Leeds were made with a single steel tube

3 feet in length and 3 inches in diameter, packed with fragments of granular refractory material, meshed to a proper size, and fitted at one end with a fire-clay plug, through which was bored a circular hole, ¾ inch in diameter, for the admission of the explosive mixture of gas and air at a speed greater than that of back firing (Fig. 9). The tube was fitted into an open trough, such as you see here on the table, in which water could be evaporated at atmospheric pressure. After the lecture my assistants will demonstrate the boiling of water in this apparatus.

Such a tube may be appropriately termed the fundamental unit of our boiler system, because boilers of almost any size may be con-

DIAGRAM OF THE FUNDAMENTAL BOILER UNIT

TOTAL HEAT TRANSMITTED = 87% OF NET CAL VALUE OF GAS
TOTAL EVAPORATION = 100 LBS WATER PER HOUR FROM AND
    AT 100°C (212°F)
MEAN EVAPORATION PER SQ FT HEATING SURFACE = 20 − 22
    LBS PER HOUR FROM AND AT 100°C (212°F)
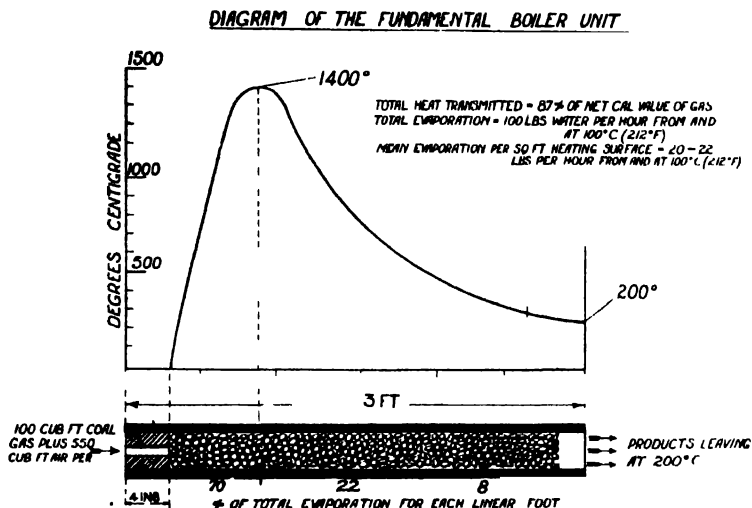
FIG 9.—DIAGRAM OF THE FUNDAMENTAL UNIT.

structed merely by multiplying the single tube, and as each tube is, so to speak, an independent fire or unit, the efficiency of the whole is that of the single tube, or in other words, the efficiency of the whole boiler is independent of the number of tubes fired.

Experimenting with such a tube, it was found possible to burn completely a mixture of 100 cubic feet of coal gas plus 550 cubic feet of air per hour, and to evaporate about 100 lb. of water from and at 100° C. (212° F.) per hour (20 to 22 lb. per square foot of heating surface), the products leaving the further end of the tube at practically 200° C. This meant the transmission to the water of 88 per cent. of the net heat developed by the combustion, and an evapora-

tion per square foot of heating surface nearly twice that of an express locomotive boiler. The combustion of the gas was completed within 4 or 5 inches of the point where it entered the tube. Of the total evaporation, no less than 70 per cent occurred over the first linear foot of the tube, 22 per cent over the second foot, and only 8 per cent. over the last foot This points to a very effective " radiation " transmission from the incandescent granular material in the first third of the tube, where the zone of active combustion is located, although it should be remarked that the *loci* of actual contact between the incandescent material and the walls of the tube are so

Pressure
17 3" W G

Pressure 2' W G

Hot Feed
Temp. 58° C

Cold Feed
Temp 5 5° C
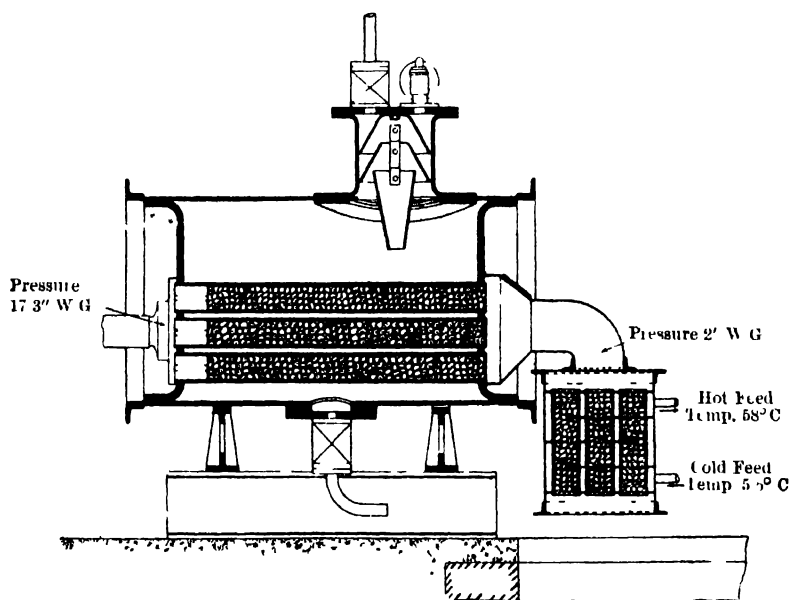
FIG 10.

rapidly cooled by the transmission of heat to the water on the other side that they never attain a temperature even approaching red heat. The granular material in the remaining two-thirds of the tube serves to baffle the hot products of combustion, and to make them repeatedly impinge with high velocity against the walls of the tube, thus materially accelerating their cooling, and either preventing or minimising the formation of the feebly-conducting stationary film of relatively cold gases which in ordinary boiler practice clings to the tube walls, seriously impairing the heat transmission.

Having thus satisfied ourselves of the efficiency of the funda-

mental unit as an evaporator, we proceeded to construct our first experimental boiler, made up of ten tubes, each 3 ft. long and 3 in. in diameter, fixed horizontally in a cylindrical steel shell capable of withstanding a pressure of over 200 lb. per square inch. This boiler is shown diagrammatically in Fig. 10 (section showing three tubes only), whilst Fig. 11 is a photograph of it (back view showing feed water heater). The gaseous mixture was forced through the tubes under pressure from a special feeding chamber attached to the front plate of the boiler; the products of combustion, after leaving the boiler, passed through a small feed-water heater containing nine tubes, each 1 ft. long and 3 in. in diameter, filled with granular material to facilitate the exchange of heat.

This combination of boiler and feed-water heater proved phenomenally successful in every way; in a trial run at Leeds on December 8, 1910, with coal gas of net calorific value 562 B.Th.Us. per cubic foot at N.T.P., and evaporating at the rate of 21·6 lb. of water from and at 212° F. per sq. ft. of heating surface per hour, the ratio of the heat utilized to the net heat developed in the tubes was 0·943. But this remarkable result was eclipsed in another independent trial carried out by German Engineers in London on January 8, 1913, when with coal gas of net calorific value 510 B.Th.Us. per cubic foot at N.T.P., and evaporating at the enormously high rate of 33·9 lb. from and at 212° F. per square foot of heating surface, the ratio of the heat utilized to the net heat developed by combustion was 0·933. The details of these tests are shown below : —

	I Dec 8, 1910	II Jan 8, 1913
1. Net cal. value of gas: B. Th. Us. per cub. ft at N. T. P.	562	510
2. Rate of evaporation: Lbs. of water per sq. ft. heating surface per hour (from and at 212° Fahr.)	21·6	33·9
3. Pressure of gaseous mixture entering the tubes · Inches W. G.	17·3	40·9
4. Pressure of products entering the feed water heater. Inches W. G.	2·0	5·14
5. Steam gauge pressure: Lbs. above atmospheric ...	100	103
6. Boiling point of the water : Fahr. Degrees	338	340°
7. Temperature products leaving boiler. Fahr. Degrees	446°	534°
8. Temperature products leaving feed water heater : Fahr. Degrees	203°	289°
9. Net heat supplied to the boiler per hour : B. Th. Us.	559,800	738,333
10. Net heat transmitted per hour: B. Th. Us.	527,800	680,000
Efficiency Ratio	0·943	0·933
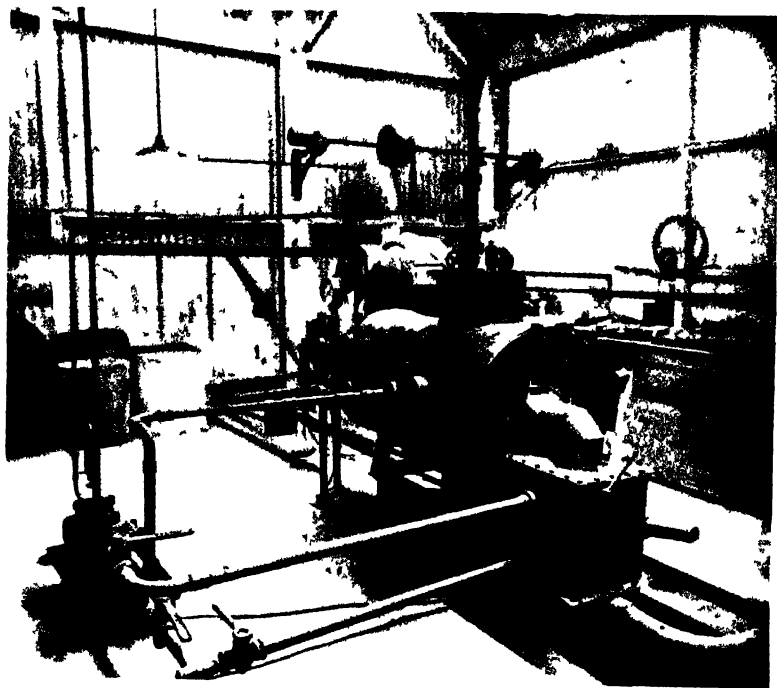
Fig 11
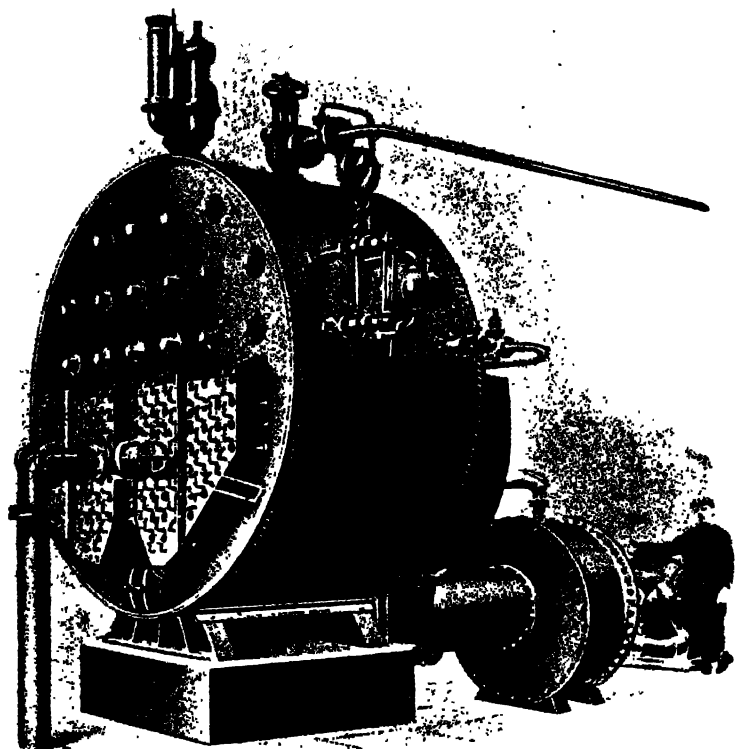
FIG. 12.

The 110-Tube Boiler at the Skinningrove Ironworks.

Six months' continuous experience with our first experimental unit gave us great confidence in its reliability, so that when in the early months of 1911 we received an inquiry from the Skinningrove Iron Co., Ltd., for a boiler of about ten times the capacity of the experimental unit, to be fired by means of the surplus gas from their new Otto by-product coking-plant, we had no hesitation in accepting a commission to instal our first large boiler there, under a strict guarantee as to its output and efficiency. This boiler (Fig. 12) was built by Messrs. Richardsons and Westgarth, Ltd., of Middlesbrough, to the design of Mr. Michael Longridge, to whom I had been
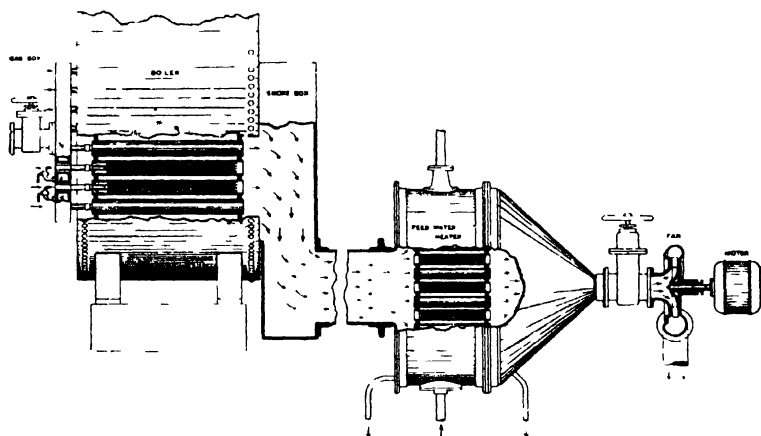
FIG. 13

indebted for much valuable advice and encouragement during the earlier experiments. It consists of a cylindrical drum 10 feet in diameter and 4 feet from front to back, traversed by 110 steel tubes, each of 3 inches internal diameter, which are packed with fragments of suitable refractory granular material. To the front of the boiler is attached a specially designed feeding chamber which delivers washed coke oven gas at 60 to 70° Fahr., and under a pressure of 1 to 2 inches W.G., to each of the 110 combustion tubes ; this gas, together with a regulated proportion of air from the outside atmosphere, is drawn, under suction from a fan, through a short mixing tube, into each of the said combustion tubes, where it is burnt

without flame in contact with the incandescent granular material. The products of combustion having traversed the 4-foot length of packed tube, pass outwards into a semicircular chamber at the back of the boiler, and thence through a duct to the tubular feed-waste heater. The fan which is attached just beyond this feed-water heater and is driven by a three phase A.C. electric motor, sucks out the cooled products, at a temperature of 100° C. (212° F.) or under, and discharges them, through a short vertical duct, into the atmosphere. The arrangement of the whole plant is shown in the accompanying diagram (Fig. 13).

The plant was successfully started up on November 7th, 1911, for a month's trial run—day and night continuously—after which it was opened up for an official inspection by the representative of a Boiler Insurance Company. Everything worked without a hitch during this trial ; steam was generated at 100 lbs. gauge pressure, from a feed-water of about four degrees of hardness, whilst the average temperature of the waste gases leaving the feed-water heater was reduced to 80° C. (say 175 Fahr.), a sure indication of the high thermal efficiency of the plant. When, at the conclusion of the month's trial, the boiler was opened up for inspection, the combustion tubes were found to be in good condition and free from scale : indeed, owing to the extremely high rate of evaporation, the scaling troubles experienced with other types of multi-tubular boilers appear to be completely obviated, the scale being automatically and continuously shed from the tube in thin films (about $\frac{1}{10}$ in. thick) as fast as it is formed ; a very important advantage, as anyone who is plagued by scaling troubles will appreciate.

After this official inspection, the plant, having amply fulfilled our guarantee, was taken over by the Skinningrove Iron Co., and it was at once re-started under the direction of Mr. E. Bury, M.Sc., the Manager of the Coke Oven Plant, who maintained it in continuous commission for three months until the great coal-strike of 1912 brought everything to a standstill.

At the end of July, 1912, after altogether five months actual running, exhaustive trials were made under the personal superintendence of an eminent American steam engineer who had crossed the Atlantic with a commission to investigate the boiler ; he subsequently reported the following results of a ten-hours' steam trial on July 29th, which speak for themselves.

RESULTS OF STEAM TRIAL, JULY 29, 1912.

Duration of test in hours   10
Mean steam gas pressure, lbs. per sq. in. above
    atmospheric   ... ...   97·2
Total gas burnt, cub. ft. at N.T.P.   101,853

Net cal. value of gas, B. Th. Us. per cub. ft. at N.T.P.   510·5*

Total net heat supplied, B. Th. Us.   52,003,996

Temperature of products leaving boiler, Fahr.
Degrees   ...   .   386° (196'' C.)

Temperature of products leaving feed-water heater,
Fahr. Degrees ...   .   202° (94·6° C.)

Total water evaporated, lbs. from and at 212° Fahr.   49,824

Evaporation in lbs. per sq. ft. of heating surface per
hour ...   .   14·1

Per cent. Dryness of steam ...   .   99·3

Total heat utilized, B. Th. Us.   48,208,399

$$\text{Ratio} \quad \frac{\text{Heat utilized}}{\text{Net heat supplied}} = 0\cdot927 \dagger$$

Power taken by fan } = 6097 watts = (say) 8·2 H.P.
[Suction = 20 in. W.G.] }

The heat balance of the test is as follows, and for purposes of comparison I will give the heat balance for a trial of a marine boiler fired with a good steam coal of net calorific value 13,800 B.Th.Us. per lb. (volatile matter = 16·1 per cent).

	Gas-Fired Surface Combustion Boiler	Coal-Fired Marine Boiler
	Per Cent	Per Cent.
Heat utilized	92·7‡	75·1
Heat lost { in burnt gases	3·0	18·1
in unburnt gases	nil	2·8
by radiation, etc.	4·3	4·0
	100·0	100·0
Rate of Evaporation in lbs. per sq. ft. heating surface per hour...	14·1	4·3

The engineer who superintended these trials was very anxious to find out whether, in view of the intensity of the combustion and the

---

* *An analysis of a typical sample of the gas gave* —
$CO_2 = 2\cdot5$; $CO = 6\ 5$, $C_nH_{2n} = 3\cdot2$; $CH_4 = 28\cdot0$;
$H_2 = 48\cdot0$; N_2, etc. = 11·3 per cent.
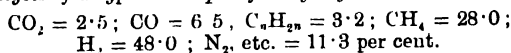
† It should be stated that the boiler was *not lagged* during the trial, otherwise this figure would have been about 0·94.

‡ Deducting the steam equivalent of the power consumed in driving the fan on the Skinningrove boiler, the "*over-all efficiency*" of the plant is *practically* 90 *per cent*. To complete the comparison, the coal-fired boiler should be similarly debited with the power (whether human or mechanical) expended in stoking.

high rate of heat transmission, the boiler tubes after five months continuous running day and night would show any signs of deterioration. Consequently, one of the boiler tubes, selected by him, was cut out and subjected to severe mechanical tests, similar tests being simultaneously made with a new and unused boiler tube of same dimensions. The results proved conclusively that the five months' service had not in any way impaired the mechanical properties of the boiler tubes, thus falsifying the confident predictions of several critics that the tubes would be speedily burnt through :—

	New Tube	Old Tube after 5 Months Service	
		Front End of Boiler	Back end of Boiler
Ultimate tensile strength, tons per per sq. in.	25·3–27·1	27·9–29·6	29·7–31·6
Elastic limit	11·9–14·4	20·05	19·3–20·5
Per cent elongation on 8 in. length	23–24	19–21	18–23
Per cent area contraction	55·6–58·8	61·3–63·1	53·4–61·3

The new tube was slightly thinner than the old one, and therefore the better comparison would be between the results obtained for the specimens taken from the *front* and *back* ends of the old tube, because, whereas the specimen from the front end had surrounded the intensely heated "zone of combustion," that from the back end had never been subjected to a higher temperature than that of the water in the boiler (say 168° C. or 335° F.). The results of the tests show practically no difference between the mechanical strengths of the two specimens. Perhaps the best testimonial to the success of this initial installation of a large boiler on the new principle is the fact that the Skinningrove Iron Co. have put down a second unit for their new battery of coke ovens, which is now being started up, and I expect, within a few weeks at most, to see the two boilers working side by side.

Within the last few months the firm of Krupps have put down a boiler in connection with one of their coking plants in the Ruhr district of Westphalia, from the plans of the Skinningrove plant. This boiler has been running successfully since October last, and about three weeks ago underwent its official steam trials, which were carried out by the Bergbauliche Verein. Pending the official publication of the results in the German technical press, I am precluded from giving any details to-night, but an unofficial test on October 30th, 1913, showed a total evaporation of 6750 lb. of water "from and at 212° Fahr." per hour, with an efficiency ratio of

0·925 ; and I am informed that the results of the recent official tests have confirmed these satisfactory figures.

As this is the first occasion on which I have been able to refer in public to the successful inauguration of these inventions on a commercial scale in Germany, and in anticipation of the publication of the results of the official German trial, I wish, with your kind permission, to mention a matter which, although it may appear personal, is nevertheless bound up with the credit of British scientific invention.

This boiler, invented and developed as it was in Leeds, by a group of British chemists, all University trained men, aided by the advice of Mr. Michael Longridge and by the enterprise of my friends of the Skinningrove Iron Co., may truly be claimed as an "all-British" invention, if ever there was one. Nevertheless, it has recently been described in the German technical press as the "Bone Schnabel," or the "Schnabel Bone" boiler, instead of the "Bonecourt" boiler, as it should be. It may be necessary at some future time, to deal more fully with this aspect of the matter, but to-night I will content myself with a protest against any attempt to claim or represent this boiler as, in part, a German invention.

I have perhaps said enough already about the boiler and its working to convince you that it combines high thermal efficiency and concentration of power, in a unique degree, and perhaps I may be permitted to summarize the other important advantages which may be claimed for it. *Firstly*, from the constructional point of view, nothing could be simpler or more compact than a cylindrical shell only 4 feet long by 10 feet in diameter, traversed by straight tubes, supported on a casting, and requiring neither elaborate brickwork setting nor expensive chimney flues and stack. *Secondly*, it has a further advantage over all multitubular boilers in that the front plate can never be heated beyond the temperature of the water, however much the firing may be forced, a circumstance which, coupled with the extremely short length of the tubes, implies an absence of strain and greatly reduces the risk of leaky joints. *Thirdly*, the high rate of mean evaporation obviates scaling troubles, and the very steep evaporation gradient along each tube causes a considerable natural circulation of water in the boiler, a factor of great importance from the point of view of good and efficient working ; in this connection I may remind you that under normal working conditions we obtain a *mean evaporation* of 20 lbs. per square foot of heating surface per hour, and can, if need be, force this up to 35 lbs. ; of this total evaporation, 70 per cent occurs over the first *third* length of the tube, 22 per cent over the *second* third, and only 8 per cent over the last third. *Fourthly*, inasmuch as each tube of the boiler is, so to speak, an independent combustion unit, capable of being shut off or lit up without affecting the others, and as it only takes five minutes after lighting up a cold tube to attain its maximum steam output, it is

obvious that not only is such a boiler highly responsive to rapid variations in the load, but also it works with equal efficiency at both small and big loads ; indeed, within very wide limits, its efficiency is practically independent of the load.

I have endeavoured, within the hour, to trace the history of an idea from its inception in the laboratory through its experimental stages right up to its successful technical applications.   Modern chemistry originated in the primeval instinct of " fire-worship," and even a century after Davy's work, the science of combustion is not yet a completed record.   On the theoretical side, there are still obscure points concerning the mechanism of " surface combustion " for future investigation, and it will probably take many years to realize the wide range of industrial possibilities in gas-firing already opened up, not to speak of the equally important problem of " oil-firing."   The number of applications of " surface combustion " which have been pressed upon our attention from without is positively embarrassing, and the task of fulfilling all expectations in the near future is indeed formidable.   I hope, however, I have succeeded in convincing you that a sound foundation has been laid, upon which may be reared an enduring edifice.

[W. A. B.]

Friday, March 20, 1914.

ALEXANDER SIEMENS, Esq., M.Inst.C.E. M.I.E.E., Secretary
and Vice-President, in the Chair.

THE RIGHT HON. LORD RAYLEIGH, O.M. P.C. LL.D. D.Sc. F.R.S.
M.R.I., Honorary Professor of Natural Philosophy,
Royal Institution.

Fluid Motions.

THE subject of this lecture has received the attention of several
generations of mathematicians and experimenters. Over a part of
the field their labours have been rewarded with a considerable degree
of success. In all that concerns small vibrations, whether of air,
as in sound, or of water, as in waves and tides, we have a large body
of systematized knowledge, though in the case of the tides the question
is seriously complicated by the fact that the rotation of the globe is
actual and not merely relative to the sun and moon, as well as by
the irregular outlines and depths of the various oceans. And even
when the disturbance constituting the vibration is not small, some
progress has been made, as in the theory of sound waves in one
dimension, and of the tidal *bores*, which are such a remarkable
feature of certain estuaries and rivers.

The general equations of fluid motions, when friction or viscosity
is neglected, were laid down in quite early days by Euler and
Lagrange, and in a sense they should contain the whole theory. But,
as Whewell remarked, it soon appeared that these equations by
themselves take us a surprisingly little way, and much mathematical
and physical talent had to be expended before the truths hidden in
them could be brought to light and exhibited in a practical shape.
What was still more disconcerting, some of the general propositions so
arrived at were found to be in flagrant contradiction with observa-
tion, even in cases where at first sight it would not seem that viscosity
was likely to be important. Thus a solid body, submerged to a
sufficient depth, should experience no resistance to its motion through
water. On this principle the screw of a submerged boat would be
useless, but, on the other hand, its services would not be needed. It
is little wonder that practical men should declare that theoretical
hydrodynamics has nothing at all to do with real fluids. Later we
will return to some of these difficulties, not yet fully surmounted, but

for the moment I will call your attention to simple phenomena of which theory can give a satisfactory account.

Considerable simplification attends the supposition that the motion is always the same at the same place—is *steady*, as we say—and fortunately this covers many problems of importance. Consider the flow of water along a pipe whose section varies. If the section were uniform, the pressure would vary along the length only in consequence of friction, which now we are neglecting. In the proposed pipe how will the pressure vary? I will not prophesy as to a Royal Institution audience, but I believe that most unsophisticated people suppose that a contracted place would give rise to an *increased* pressure. As was known to the initiated long ago, nothing can be further from this fact. The experiment is easily tried, either with air or water, so soon as we are provided with the right sort of tube. A suitable shape is shown in Fig. 1, but it is rather trouble-
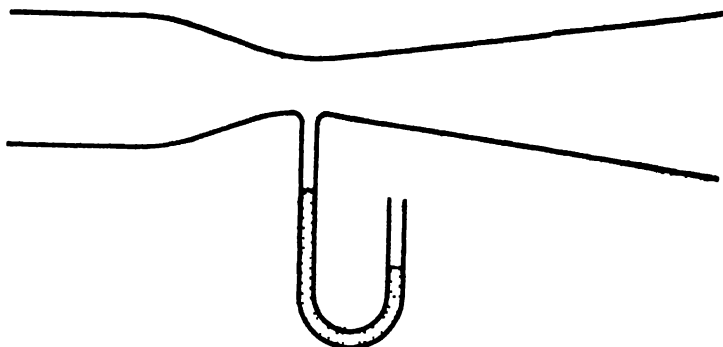
FIG 1.

some to construct in metal. W. Froude found paraffin-wax the most convenient material for ship models, and I have followed him in the experiment now shown. A brass tube is filled with candle-wax and bored out to the desired shape, as is easily done with templates of tin plate. When I blow through, a *suction* is developed at the narrows, as is witnessed by the rise of liquid in a manometer connected laterally.

In the laboratory, where dry air from an acoustic bellows or a gas-holder is available, I have employed successfully tubes built up of cardboard, for a circular cross-section is not necessary. Three or more precisely similar pieces, cut for example to the shape shown in Fig. 2 and joined together closely along the edges, give the right kind of tube, and may be made air-tight with pasted paper or with sealing-wax. Perhaps a square section requiring four pieces is best. It is worth while to remark that there is no stretching of the card-

board, each side being merely *bent* in one dimension. A model is before you, and a study of it forms a simple and useful exercise in solid geometry.

Another form of the experiment is perhaps better known, though
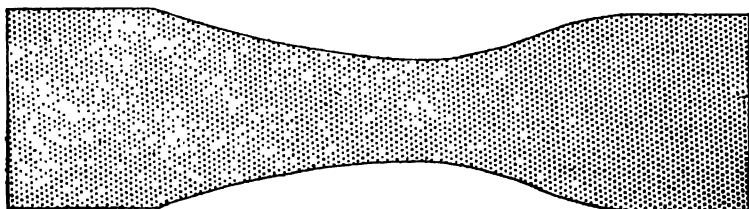
FIG. 2.

rather more difficult to think about. A tube (Fig. 3) ends in a flange. If I blow through the tube, a card presented to the flange is drawn up pretty closely, instead of being blown away as might be expected. When we consider the matter, we recognize that the channel between the flange and the card through which the air flows after leaving the tube is really an expanding one, and thus that the inner part may fairly be considered as a contracted place. The suction here developed holds the card up.
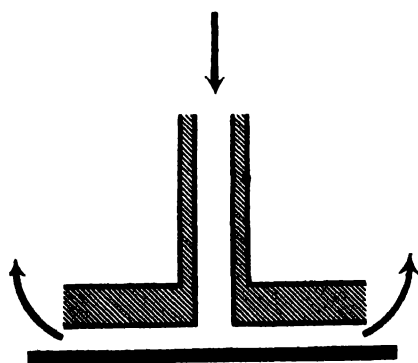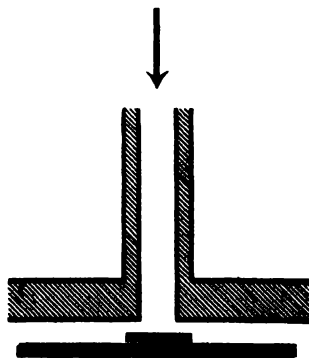
FIG. 3.   FIG. 4

A slight modification enhances the effect. It is obvious that immediately opposite the tube there will be pressure upon the card and not suction. To neutralize this a sort of cap is provided, attached to the flange, upon which the objectionable pressure is taken (Fig. 4). By blowing smartly from the mouth through this little apparatus it is easy to lift and hold up a penny for a short time.

The facts then are plain enough, but what is the explanation ?   It is really quite simple.   In steady motion the quantity of fluid per second passing any section of the tube is everywhere the same.   If the fluid be incompressible, and air in these experiments behaves pretty much as if it were, this means that the product of the velocity and area of cross-section is constant, so that at a narrow place the velocity of flow is necessarily increased.   And when we enquire how the additional velocity in passing from a wider to a narrower place is to be acquired, we are compelled to recognize that it can only be in consequence of a fall of pressure.   The suction at narrows is the only result consistent with the great principle of conservation of energy ; but it remains rather an inversion of ordinary ideas that we should have to deduce the forces from this motion, rather than the motion from the forces.

The application of the principle is not always quite straight-forward.   Consider a tube of slightly conical form, open at both ends, and suppose that we direct upon the narrower end a jet of air from a tube having the same (narrower) section (Fig 5).   We might expect
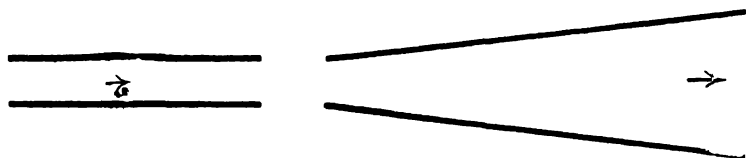
F_{IG}. 5

this jet to enter the conical tube without much complication.   But if we examine more closely a difficulty arises.   The stream in the conical tube would have different velocities at the two ends, and therefore different pressures.   The pressures at the ends could not both be atmospheric.   Since at any rate the pressure at the wider delivery end must be very nearly atmospheric, that at the narrower end must be decidedly below that standard.   The course of the events at the inlet is not so simple as supposed, and the apparent contradic-tion is evaded by an inflow of air from outside, in addition to the jet, which assumes at entry a narrower section.

If the space surrounding the free jet is enclosed (Fig. 6), suction is there developed, and ultimately when the motion has become steady the jet enters the conical tube without contraction.   A model shows the effect, and the principle is employed in a well-known laboratory instrument arranged for working off the water-mains.

I have hitherto dealt with air rather than water, not only because air makes no mess, but also because it is easier to ignore gravitation. But there is another and more difficult question.   You will have noticed that in our expanding tubes the section changes only gradu-ally.   What happens when the expansion is more sudden—in the

extreme case when the diameter of a previously uniform tube suddenly becomes infinite ?   (Fig. 3 without card.)   Ordinary experience teaches that in such a case the flow does not follow the walls round the corner, but shoots across as a jet, which for a time preserves its individuality and something like its original section.   Since the velocity is not lost, the pressure which would replace it is not developed. It is instructive to compare this case with another, experimented on by Savart * and W. Froude,† in which a free jet is projected through a short cone, or a mere hole in a thin wall, into a vessel under a higher pressure.   The apparatus consists of two precisely similar vessels with apertures, in which the fluid (water) may be at different levels (Fig. 7, copied from Froude).   Savart found that not a single drop of liquid was spilt so long as the pressure in the recipient vessel did not exceed one-sixth of that under which the jet issues.   And Froude reports that so long as the head in the discharge cistern is
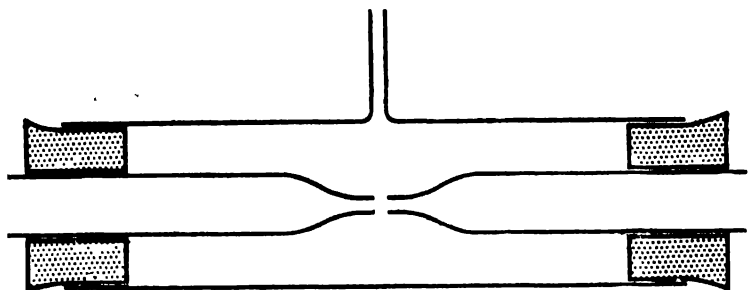
Fig. 6.

maintained at a moderate height above that in the recipient cistern, the whole of the stream enters the recipient orifice, and there is " no waste, except the small sprinkling which is occasioned by inexactness of aim, and by want of exact circularity in the orifices." I am disposed to attach more importance to the small spill, at any rate when the conoids are absent or very short.   For if there is no spill, the jet (it would seem) might as well be completely enclosed : and then it would propagate itself into the recipient cistern without sudden expansion and consequent recovery of pressure.   In fact, the pressure at the narrows would never fall below that of the recipient cistern, and the discharge would be correspondingly lessened.   When a decided spill occurs, Froude explains it as due to the retardation by friction of the outer layers, which are thus unable to force themselves against the pressure in front.

Evidently it is the behaviour of these outer layers, especially at

* Ann. de Chimie, lv. p. 257, 1833.
† Nature, vol. iii. p. 93, 1875.

narrow places, which determines the character of the flow in a large
variety of cases. They are held back, as Froude pointed out, by
friction acting from the walls ; but, on the other hand, when they
lag they are pulled forward by layers farther in which still retain
their velocity. If the latter prevail, the motion in the end may not
be very different from what would occur in the absence of friction ;
otherwise an entirely altered motion may ensue. The situation as
regards the rest of the fluid is much easier when the layers upon
which the friction tells most are allowed to escape. This happens in
instruments of the injector class, but I have sometimes wondered
whether full advantage is taken of it. The long gradually expanding
cones are overdone, perhaps, and the friction which they entail must
have a bad effect.
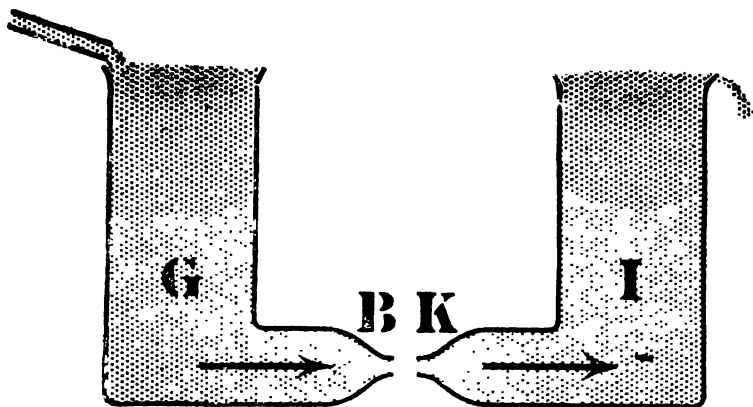
Fig. 7.

Similar considerations enter when we discuss the passage of a
solid body through a large mass of fluid otherwise at rest, as in the
case of an airship or submarine boat. I say a submarine, because
when a ship moves upon the surface of the water the formation
of waves constitutes a complication, and one of great importance
when the speed is high. In order that the water in its relative
motion may close in properly behind, the after-part of the ship must
be suitably shaped, fine lines being more necessary at the stern than
at the bow, as fish found out before men interested themselves in the
problem. In a well-designed ship the whole resistance (apart from
wave-making) may be ascribed to *skin friction*, of the same nature as
that which is encountered when the ship is replaced by a thin plane
moving edgeways.

At the other extreme we may consider the motion of a thin disk
or blade flatways through the water. Here the actual motion differs

altogether from that prescribed by the classical hydro-dynamics, according to which the character of the motion should be the same behind as in front. The liquid refuses to close in behind, and a region of more or less "dead water" is developed, entailing a greatly increased resistance. To meet this Helmholtz, Kirchhoff, and their followers have given calculations in which the fluid behind is supposed to move strictly with the advancing solid, and to be separated from the remainder of the mass by a surface at which a finite slip takes place. Although some difficulties remain, there can be no doubt that this theory constitutes a great advance. But the surface of separation is unstable, and in consequence of fluid friction it soon loses its sharpness, breaking up into more or less periodic eddies, described in some detail by Mallock (Fig. 8). It is these eddies which cause the whistling of the wind in trees and the more musical notes of the æolian harp.

The obstacle to the closing-in of the lines of flow behind the disk is doubtless, as before, the layer of liquid in close proximity to
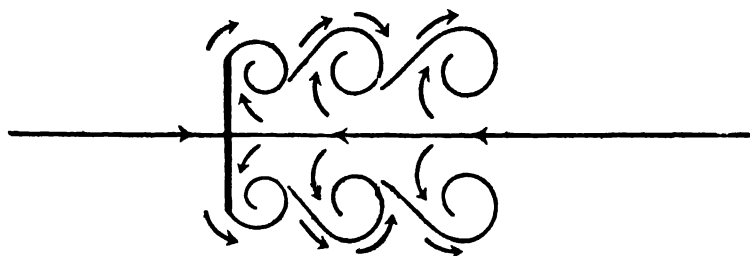
FIG. 8.

the disk, which at the edge has insufficient velocity for what is required of it. It would be an interesting experiment to try what would be the effect of allowing a small "spill." For this purpose the disk or blade would be made double, with a suction applied to the narrow interspace. Relieved of the slowly moving layer, the liquid might then be able to close in behind, and success would be witnessed by a greatly diminished resistance.

When a tolerably fair-shaped body moves through fluid, the relative velocity is greatest at the maximum section of the solid which is the minimum section for the fluid, and consequently the pressure is there least. Thus the water-level is depressed at and near the midship section of an advancing steamer, as is very evident in travelling along a canal. On the same principle may be explained the stability of a ball sustained on a vertical jet as in a well-known toy (shown). If the ball deviate to one side, the jet in bending round the surface develops a suction pulling the ball back. As Mr. Lanchester has remarked, the effect is aided by the rotation of the

ball. That a convex surface is attracted by a jet playing obliquely upon it was demonstrated by T. Young more than 100 years ago by means of a model, of which a copy is before you (Fig. 9).

It has been impossible in dealing with experiments to keep quite clear of friction, but I wish now for a moment to revert to the ideal fluid of hydro-dynamics, in which pressure and inertia alone come into account. The possible motions of such a fluid fall into two great classes—those which do and those which do not involve *rotation*. What exactly is meant by rotation is best explained after the manner of Stokes. If we imagine any spherical portion of the fluid in its motion to be suddenly solidified, the resulting solid may be found to be rotating. If so, the original fluid is considered to possess rotation. If a mass of fluid moves irrotationally, no spherical
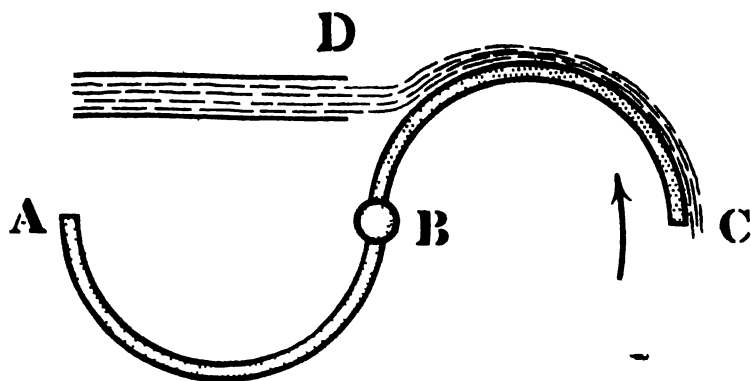
Fig. 9.

A plate, bent into the form A, B, C, turning on centre B, is impelled by a stream of air D in the direction shown

portion would revolve on solidification   The importance of the distinction depends mainly upon the theorem, due to Lagrange and Cauchy, that the irrotational character is permanent, so that any portion of fluid at any time destitute of rotation will always remain so. Under this condition fluid motion is comparatively simple, and has been well studied. Unfortunately many of the results are very unpractical.

As regards the other class of motions, the first great step was taken in 1858, by Helmholtz, who gave the theory of the vortex-ring. In a perfect fluid a vortex-ring has a certain permanence and individuality, which so much impressed Kelvin that he made it the foundation of a speculation as to the nature of matter. To him we owe also many further developments in pure theory.

On the experimental side, the first description of vortex-rings

that I have come across is that by W. B. Rogers,[*] who instances their production during the bursting of bubbles of phosphuretted hydrogen, or the escape of smoke from cannon and from the lips of expert tobacconists. For private observation nothing is simpler than Helmholtz's method of drawing a partially immersed spoon along the surface, for example, of a cup of tea. Here half a ring only is developed, and the places where it meets the surface are shown as dimples, indicative of diminished pressure. The experiment, made on a larger scale, is now projected upon the screen, the surface of the liquid and its motion being made more evident by powder of lycopodium or sulphur scattered over it. In this case the ring is generated by the motion of a half-immersed circular disk, withdrawn after a travel of two or three inches. In a modified experiment the disk is replaced by a circular or semi-circular *aperture* cut in a larger plate, the level of the water coinciding with the horizontal diameter of the aperture. It may be noticed that while the first forward motion of the plate occasions a ring behind, the stoppage of the plate gives rise to a second ring in front. As was observed by Reusch,[†] the same thing occurs in the more usual method of projecting smoke-rings from a box ; but in order to see it the box must be transparent.

In a lecture given here in 1877, Reynolds showed that a Helmholtz ring can push the parent disk before it, so that for a time there appears to be little resistance in its motion.

For an explanation of the origin of these rings we must appeal to friction, for in a perfect fluid no rotation can develop. It is easy to recognize that friction against the wall in which the aperture is perforated, or against the face of the disk in the other form of experiment, will start a rotation which, in a viscous fluid, such as air or water actually is, propagates itself to a finite distance inwards. But although a general explanation is easy, many of the details remain obscure.

It is apparent that in dealing with a large and interesting class of fluid motions we cannot go far without including fluid friction, or viscosity as it is generally called, in order to distinguish it from the very different sort of friction encountered by solids, unless well lubricated. In order to define it, we may consider the simplest case where fluid is included between two parallel walls, at unit distance apart, which move steadily, each in its own plane, with velocities which differ by unity. On the supposition that the fluid also moves in plane strata, the viscosity is measured by the tangential force per unit of area exercised by each stratum upon its neighbours When we are concerned with internal motions only, we have to do rather with the so-called " kinematic viscosity," found by dividing the quantity above defined by the density of the fluid. On this system the viscosity of water is much *less* than that of air.

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* Amer. J. Sci., vol. xxvi. p. 246, 1858.
† Pogg. Ann., vol. cx. p. 309, 1860.

Viscosity varies with temperature ; and it is well to remember that the viscosity of air increases while that of water decreases as the temperature rises. Also that the viscosity of water may be greatly increased by admixture with alcohol. I used these methods in 1879 during investigations respecting the influence of viscosity upon the behaviour of such fluid jets as are sensitive to sound and vibration.

Experimentally the simplest case of motion in which viscosity is paramount is the flow of fluid through capillary tubes. The laws of such motion are simple, and were well investigated by Poiseuille. This is the method employed in practice to determine viscosities. The apparatus before you is arranged to show the diminution of viscosity with rising temperature. In the cold the flow of water through the capillary tube is slow, and it requires sixty seconds to fill a small measuring vessel. When, however, the tube is heated by passing steam through the jacket surrounding it, the flow under the same head is much increased, and the measure is filled in twenty-six seconds. Another case of great practical importance, where viscosity is the leading consideration, relates to lubrication. In admirably conducted experiments Tower showed that the solid surfaces moving over one another should be separated by a complete film of oil, and that when this is attended to there is no wear. On this basis a fairly complete theory of lubrication has been developed, mainly by O. Reynolds. But the capillary nature of the fluid also enters to some extent, and it is not yet certain that the whole character of a lubricant can be expressed even in terms of both surface tension and viscosity.

It appears that in the extreme cases, when viscosity can be neglected and again when it is paramount, we are able to give a pretty good account of what passes. It is in the intermediate region, where both inertia and viscosity are of influence, that the difficulty is greatest. But even here we are not wholly without guidance. There is a general law, called the law of dynamical similarity, which is often of great service. In the past this law has been unaccountably neglected, and not only in the present field. It allows us to infer what will happen upon one scale of operations from what has been observed at another. On the present occasion I must limit myself to viscous fluids, for which the law of similarity was laid down in all its completeness by Stokes as long ago as 1850. It appears that similar motions may take place provided a certain condition be satisfied, viz. that the product of the linear dimension and the velocity, divided by the kinematic viscosity of the fluid, remain unchanged. Geometrical similarity is pre-supposed. An example will make this clearer. If we are dealing with a single fluid, say air under given conditions, the kinematic viscosity remains of course the same. When a solid sphere moves uniformly through air, the character of the motion of the fluid round it may depend upon the size of the sphere and upon the velocity with which it travels. But we may infer that the motions remain *similar*, if only

the product of diameter and velocity be given. Thus, if we know the motion for a particular diameter and velocity of the sphere, we can infer what it will be when the velocity is halved and the diameter doubled. The fluid velocities also will everywhere be halved at the *corresponding* places. M. Eiffel found that for any sphere there is a velocity which may be regarded as critical, i.e. a velocity at which the law of resistance changes its character somewhat suddenly. It follows from the rule that these critical velocities should be inversely proportional to the diameters of the spheres, a conclusion in pretty good agreement with M. Eiffel's observations.* But the principle is at least equally important in effecting a comparison between different fluids. If we know what happens on a certain scale and at a certain velocity in *water*, we can infer what will happen in *air* on any other scale, provided the velocity is chosen suitably. It is assumed here that the compressibility of the air does not come into account, an assumption which is admissible so long as the velocities are small in comparison with that of sound.

But although the principle of similarity is well established on the theoretical side and has met with some confirmation in experiment, there has been much hesitation in applying it, due perhaps to certain discrepancies with observation which stand recorded. And there is another reason. It is rather difficult to understand how viscosity can play so large a part as it seems to do, especially when we introduce numbers, which make it appear that the viscosity of air, or water, is very small in relation to the other data occurring in practice. In order to remove these doubts it is very desirable to experiment with different viscosities, but this is not easy to do on a moderately large scale, as in the wind channels used for aeronautical purposes. I am therefore desirous of bringing before you some observations that I have recently made with very simple apparatus.

When liquid flows from one reservoir to another through a channel in which there is a contracted place, we can compare what we may call the *head* or driving pressure, i.e. the difference of the pressures in the two reservoirs, with the *suction*, i.e. the difference between the pressure in the recipient vessel and that lesser pressure to be found at the narrow place. The ratio of head to suction is a purely numerical quantity, and according to the principle of similarity it should for a given channel remain unchanged, provided the velocity be taken proportional to the kinematic viscosity of the fluid. The use of the same material channel throughout has the advantage that no question can arise as to geometrical similarity, which in principle should extend to any roughnesses upon the surface, while the necessary changes of velocity are easily attained by altering the head and those of viscosity by altering the temperature.

* Comptes Rendus, Dec. 30, 1912 ; Jan. 13, 1913.

The apparatus consisted of two aspirator bottles (Fig. 10) containing water and connected below by a passage bored in a cylinder of lead, 7 cm. long, fitted water-tight with rubber corks. The form of channel' actually employed is shown in Fig. 11. On the upstream side it contracts pretty suddenly from full bore (8 mm.) to the narrowest place, where the diameter is 2·75 mm. On the downstream side the expansion takes place in four or five steps, corresponding to the drills available. It had at first been intended to use a smooth curve, but preliminary trials showed that this was unnecessary, and the expansion by steps has the advantage of bringing
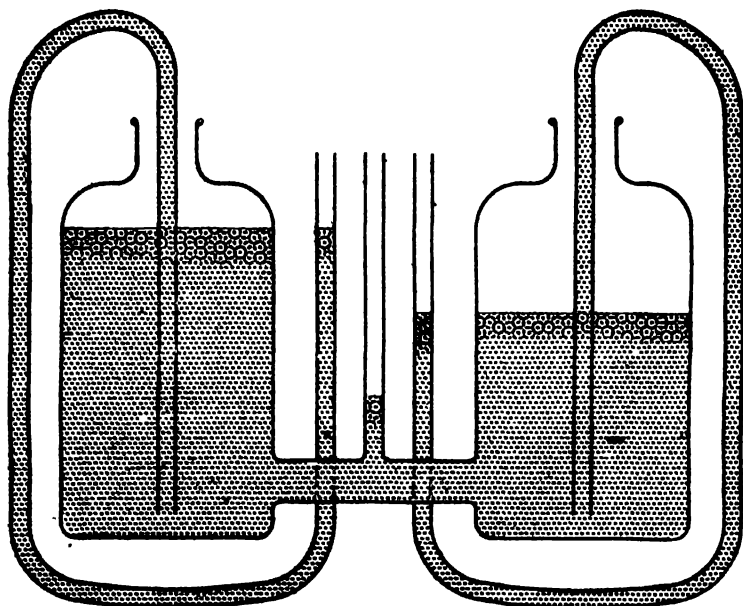
FIG. 10.

before the mind the dragging action of the jets upon the thin layers of fluid between them and the walls. The three pressures concerned are indicated on manometer tubes as shown, and the two differences of level representing head and suction can be taken off with compasses and referred to a millimetre scale. In starting an observation the water is drawn up in the discharge vessel, as far as may be required, with the aid of an air-pump. The rubber cork at the top of the discharge vessel necessary for this purpose is not shown.

As the head falls during the flow of the water, the ratio of head to suction increases. For most of the observations I contented myself with recording the head for which the ratio of head to

suction was exactly 2 : 1, as indicated by proportional compasses. Thus on January 23, when the temperature of the water was 9° C., the 2 : 1 ratio occurred on four trials at 120, 130, 123, 126, mean 125 mm. head.   The temperature was then raised with precaution by pouring in warm water with passages backwards and forwards. The occurrence of the 2 : 1 ratio was now much retarded, the mean head being only 35 mm., corresponding to a mean temperature of 37° C.   The ratio of head to suction is thus dependent upon the head or velocity, but when the velocity is altered the original ratio may be recovered if at the same time we make a suitable alteration of viscosity.

And the required alteration of viscosity is about what might have been expected.   From Landolt's tables I find that for 9° C. the viscosity of water is ·01368, while for 37° C. it is ·00704.   The ratio of viscosities is accordingly 1·943.   The ratio of heads is 125 : 35.   The ratio of *velocities* is the square-root of this or 1·890, in sufficiently good agreement with the ratio of viscosities.
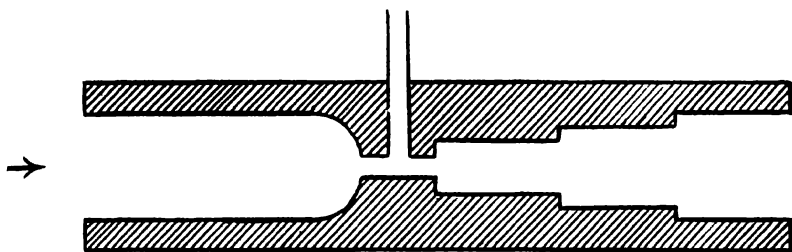
FIG. 11.

In some other trials the ratio of heads *exceeded* a little the ratio of viscosities.   It is not pretended that the method would be an accurate one for the comparison of viscosities.   The change in the ratio of head to suction is rather slow, and the measurement is usually somewhat prejudiced by unsteadiness in the suction manometer.   Possibly better results would be obtained in more elaborate observations by several persons, the head and suction being recorded separately and referred to a time scale so as to facilitate interpolation.   But as they stand the results suffice for my purpose, showing directly and conclusively the influence of viscosity as compensating a change in the velocity.

In conclusion, I must touch briefly upon a part of the subject where theory is still at fault, and I will limit myself to the simplest case of all—the uniform shearing motion of a viscous fluid between two parallel walls, one of which is at rest, while the other moves tangentially with uniform velocity.   It is easy to prove that a uniform shearing motion of the fluid satisfies the dynamical equa-

tions, but the question remains : Is this motion stable ? Does a small departure from the simple motion tend of itself to die out ? In the case where the viscosity is relatively great, observation suggests an affirmative answer ; and O. Reynolds, whose illness and comparatively early death were so great a loss to science, was able to deduce the same conclusion from theory. Reynolds' method has been improved, more especially by Professor Orr of Dublin. The simple motion is thoroughly stable if the viscosity exceed a certain specified value relative to the velocity of the moving plane and the distance between the planes ; while if the viscosity is less than this, it is possible to propose a kind of departure from the original motion which will increase *for a time.* It is on this side of the question that there is a deficiency. When the viscosity is very small, observation appears to show that the simple motion is unstable, and we ought to be able to derive this result from theory. But even if we omit viscosity altogether, it does not appear possible to prove instability *à priori,* at least so long as we regard the walls as mathematically plane. We must confess that at the present we are unable to give a satisfactory account of skin-friction, in order to overcome which millions of horse-power are expended in our ships. Even in the older subjects there are plenty of problems left !

[R.]

Friday, June 5, 1914.

CHARLES HAWKSLEY, ESQ., M.Inst.C.E., Vice-President,
in the Chair.

PROFESSOR WILLIAM H. BRAGG, M.A. F.R.S.

X-Rays and Crystalline Structure.

Two years have gone by since Dr. Laue made his surprising dis-
covery of the interference effects accompanying the passage of X-rays
through crystals. The pioneer experiment has opened the way for
many others, and a very large amount of work, theoretical and
practical, has now been done. As the preliminary exploration of
the new country has proceeded, our first estimate of its resources
has grown continuously ; we have learned many things which help us
to a better understanding of phenomena already familiar, and we
have seen avenues of enquiry open out before us which as yet there
has been little time to follow. The work is full of opportunities
for exact quantitative measurement, where precision is sure to bring
its due reward. There is enough work in sight to absorb the ener-
gies of many experimenters, and there is sure to be far more than
we can see. When we consider the wideness of the new field, the
quality and quantity of the work to be done in it, and the import-
ance of the issues, we are scarcely guilty of over-statement if we
say that Laue's experiment has led to the development of a new science.
    The experiment itself—to put it very briefly—constitutes a proof
that X-rays consist of extremely short ether waves. In order to
appreciate the value of this demonstration, we must bear in mind
the present conditions of our knowledge of the laws of radiation in
general. Let us consider very shortly how the whole matter stood
when the new work was begun.
    When X rays were first discovered eighteen years ago it was
soon pointed out that they might consist of electro-magnetic dis-
turbance of the ether analogous to those supposed to constitute light.
It was true that the new rays seemed to be incapable of reflection,
refraction, diffraction, and interference, which were familiar optical
phenomena. But it was pointed out by Schuster* that these defects
could be explained as natural consequences of an extremely small
wave-length. The positive evidence consisted mainly in the know-

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ledge that the impact of the electrons on the anti-cathode of the X-ray bulb ought to be the occasion of electro-magnetic waves of some sort, and in the discovery by Barkla that the X-rays could be polarized, which last is a property also of light.

As experimental evidence accumulated, a number of results were found which the electro-magnetic theory was unable to explain, at least in a direct and simple manner. They were mainly concerned with the transference of energy from place to place. In some way or other the swiftly moving electron of the X-ray bulb transfers its energy to the X-ray, and the X-ray in its turn communicates approximately the same quantity of energy to the electron which originates from matter lying in the track of the X-ray, and which is apparently the direct cause of all X-ray effects. Experiment seemed to indicate that X-ray energy travelled as a stream of separate entities or quanta, the energy of the quantum differing according to the quality of the X-ray. It looked at one time as if it might be the simplest plan to deny the identity in nature of X-rays and light, to describe the former as a corpuscular radiation and the latter as a wave motion. Otherwise, it seemed that the electro-magnetic hypothesis would be torn to pieces in the effort to hold all the facts together.

But it appeared on a close examination of light phenomena also, though in much less obvious fashion, that the very same effects occurred which in the case of X-rays were so difficult to explain from an orthodox point of view. In the end it became less difficult to deny the completeness of the orthodox theory than the identity in nature of light and X-rays. Modern work on the distribution of energy in the spectrum, and the dependence of specific heat upon temperature, has also led independently to the same point of view. It has been urged with great force by Planck, Einstein, and others that radiated energy is actually transferred in definite units or quanta, and not continuously ; as if we had to conceive of atoms of energy as well as of atoms of matter. Let it be admitted at once that the quantum theory and the orthodox theory appear to stand in irreconcilable opposition. Each by itself correlates great series of facts ; but they do not correlate the same series. In some way or other the greater theory must be found, of which each is a partial expression.

The new discovery does not solve our difficulty at once, but it does two very important things. In the first place, it shows that the X-rays and light are identical in nature ; in fact, it removes every difference except in respect to wave-length. The question as to the exact place where the difficulty lies is decided for us ; we are set the task of discovering how a continuous wave motion, in a continuous medium, can be reconciled with discontinuous transferences of radiation energy. Some solution there must be to this problem. The second important thing is that the new methods will surely help us on the way to find that solution. We can now examine the X-rays as

critically as we have been able to study light, by means of the spectro-
meter. The wave-length of the X-ray has emerged as a measurable
quantity. The complete range of electromagnetic radiations now lies
before us. At one end are the long waves of wireless telegraphy, in
the middle are first the waves of the infra-red detected by their heat-
ing effects, then the light waves, and then the short waves of the
ultra-violet. At the other end are the extremely short waves that
belong to X-radiation. In the comparative study of the properties
of radiation over this very wide range we must surely find the answer
to the greatest question of modern physics

So much for the general question. Let us now consider the pro-
cedure of the new investigations, and afterwards one or two applica-
tions to special lines of enquiry.

The experiment due to Laue and his collaborators Friedrich
and Knipping has already been described in this lecture room and is
now well-known. A fine pencil of X-rays passes through a thin
crystal slip and impresses itself on a photographic plate. Round the
central spot are found a large number of other spots. arranged in
a symmetrical fashion, their arrangement clearly depending on the
crystal structure. Laue had anticipated some such effect as the
result of diffraction by the atoms of the crystal. His mathematical
analysis is too complicated to be described now, and indeed it is not
in any circumstances easy to handle. It will be better to pass on at
once to a very simple method of apprehending the effect which was
put forward soon after the publication of Laue's first results. I
must run the risk of seeming to be partial if I point out the import-
ance of this advance, which was made by my son W. Lawrence Bragg.
All the recent investigations of X-ray spectra and the examination of
crystal structure and of molecular motions which have been carried
out since then have been rendered possible by the easy grasp of the
subject which resulted from the simpler conception.

Let us imagine that a succession of waves constituting X-radiation
falls upon a plane containing atoms, and that each atom is the cause
of a secondary wavelet. In a well-known manner, the secondary
wavelets link themselves together and form a reflected wave. Just so
a sound wave may be reflected by a row of palings, and very short
sound waves by the fibres of a sheet of muslin.

Suppose a second plane of atoms to lie behind the first and to be
parallel to it. The primary wave, weakened somewhat by passing
through the first plane, is again partially reflected by the second.
When the two reflected pencils join it will be of great importance
whether they fit crest to crest and hollow to hollow, or whether they
tend to destroy each other's effect. If more reflecting planes are
supposed, the importance of a good fit becomes greater and greater.
If the number is very large, then, as happens in many parallel cases in
optics, the reflected waves practically annul each other unless the
fit is perfect.

It is easily seen that the question of fit depends on how much distance a wave reflected at one plane loses in comparison with the wave which was reflected at the preceding plane : the fit will be perfect if the loss amounts to one, two, three, or more wave-lengths exactly. In its turn the distance lost depends on the spacing of the planes, that is to say, the distance from plane to plane, on the wave-length and on the angle at which the rays meet the set of planes.

The question is formally not a new one. Many years ago Lord Rayleigh discussed it in this room, illustrating his point by aid of a set of muslin sheets stretched on parallel frames. The short sound waves of a high-pitched bird-call were reflected from the set of frames and affected a sensitive flame ; and he showed how the spacing of the planes must be carefully adjusted to the proper value in relation to the length of wave and the angle of incidence. Rayleigh used the illustration to explain the beautiful colours of chlorate of potash crystals. He ascribed them to the reflection of light by a series of parallel and regularly spaced twinning planes within the crystal, the distance between successive planes bearing roughly the same proportion to the length of the reflected wave of light as the distance between the muslin sheets to the length of the wave of sound.

Our present phenomenon is exactly the same thing on a minute scale : thousands of times smaller than in the case of light, and many millions of times smaller than in the case of sound.

By the kindness of Prof. R. W. Wood I am able to show you some fine examples of the chlorate of potash crystals. If white light is allowed to fall upon one of them, the whole of it is not reflected. Only that part is reflected which has a definite wave-length or something very near to it, and the reflected ray is therefore highly coloured. The wave-length is defined by the relation already referred to. If the angle of incidence is altered, the wave-length which can be reflected is altered, and so the colour changes.

It is not difficult to see the analogy between these cases and the reflection of X-rays by a crystal. Suppose, for example, that a pencil of homogeneous X-rays meets the cube face of such a crystal as rock-salt. The atoms of the crystal can be taken to be arranged in planes parallel to that face, and regularly spaced. If the rays meet the face at the proper angle, and only at the proper angle, there is a reflected pencil. It is to be remembered that the reflection is caused by the joint action of a series of planes, which, in this case, are parallel to the face ; it is not a reflection by the face itself. The face need not even be cut truly : it may be unpolished or deliberately roughened. The reflection takes place in the body of the crystal, and the condition of the surface is of little account.

The allotment of the atoms to a series of planes parallel to the surface is not of course the only one possible. For example, in the case of a cubic crystal, parallel planes containing all the atoms of the crystal may also be drawn perpendicular to a face diagonal of the

cube, or to a cube diagonal, or in many other ways. We may cut the crystal so as to show a face parallel to any series, and then place the crystal so that reflection occurs, but the angle of incidence will be different in each case since the spacings are different. It is not necessary to cut the crystal except for convenience. If wave-length, spacing, and angle between ray and plane are rightly adjusted to each other, reflection will take place in the crystal independently of any surface arrangement.

This is the " reflection " method of explaining the Laue photograph. W. L. Bragg showed in the first place that it was legitimate, and the second that it was able to explain in the position of all the spots which Laue found upon his photographs. The different spots are reflections in different series of planes which may be drawn to contain the atoms of the crystal. The simpler conception led at once to a simpler procedure. It led to the construction of the X-ray spectrometer, which resembles an ordinary spectrometer in general form, except that the grating or prism is replaced by a crystal and the telescope by an ionization chamber and an electroscope. In use a fine pencil of X-rays is directed upon the crystal, which is steadily turned until a reflection leaps out ; and the angle of reflection is then measured. If we use different crystals or different faces of the same crystal, but keep the rays the same, we can compare the geometrical spacings of the various sets of planes. If we use the same crystal always, but vary the source of X-rays, we can analyse the latter, measuring the relative wave-lengths of the various constituents of the radiation.

We have thus acquired a double power : —1. We can compare the intervals of spacing of the atoms of a crystal or of different crystals, along various directions within the crystal ; in this way we can arrive at the structure of the crystal. 2. We can analyse the radiation of an X-ray bulb. In fact, we are in the same position as we should have been in respect to light if our only means of analysing light had been by the use of coloured glasses, and we had then been presented with a spectrometer, or some other means of measuring wave-length exactly.

We now come to a critical point. If we knew the exact spacings of the planes of some one crystal, we could now by comparison find the spacings of all other crystals, and measure the wave-length of all X-radiations ; or if we knew the exact value of some one wave-length, we could find by comparison the values of all other wave-lengths, and determine the spacings of all crystals. But as yet we have no absolute value either of wave-length or of spacings.

The difficulty appears to have been overcome by W. L. Bragg's comparison of the reflecting effect in the case of rocksalt or sodium chloride, and sylvine or potassium chloride. These two crystals are known to be " isomorphous " : they must possess similar arrangements of atoms. Yet they display a striking difference both in the Laue

photograph and on the spectrometer. The reflections from the various series of planes of the latter crystal show spacings consonant with an arrangement in the simplest cubical array, of which the smallest element is a cube at each corner of which is placed the same group, a single atom or molecule, or group of atoms or molecules. In the case of rocksalt, the indications are that the crystal possesses a structure intermediate between the very simple arrangement just described and one in which the smallest element is a cube having a similar group of atoms or molecules at every corner and at the middle point of each face. The arrangement is called by crystallographers the face-centred cube. The substitution of the sodium for the potassium atom must transform one arrangement into the other. This can be done in the following way, if we accept various indications that atoms of equal weight are to be treated as equivalent. Imagine an elementary cube of the crystal pattern to have an atom of chlorine at every corner and in the middle of each face, and an atom of sodium or potassium as the case may be, at the middle point of each edge and at the centre of the cube. We have now an arrangement which fits the facts exactly. The weights of the potassium and chlorine atoms are so nearly the same as to be practically equivalent, and when they are considered to be so, the arrangement becomes the simple cube of sylvine. But when the lighter sodium replaces the potassium as in rocksalt the arrangement is on its way to be that of the face-centred cube, and would actually become so were the weight of the sodium atoms negligible in comparison with those of chlorine. Of course the same result would follow were two or three, or any number of atoms of each sort to take the place of the single atom, provided the same increase were made in the number of the atoms of both sorts. We might even imagine two sorts of groups of chlorine and metal atoms, one containing a preponderance of the former, the other of the latter, but so that two groups, one of each kind, contain between them the same proportion of chlorine and metal as the crystal does. We must merely have two groups which differ in weight in the case of rocksalt, and are approximately equal in weight in the case of sylvine. But it was best to take the simplest supposition at the outset : and now the evidence that the right arrangement has been chosen is growing as fresh crystals are measured. For it turns out that in all crystals so far investigated, the number of atoms at each point must always be the same. Why, then, should it be more than one ? Or in other words, if atoms are always found in groups of a certain number, ought not that group to be called the atom ?

As soon as the structure of a crystal has been found we can at once find by simple arithmetic the scale on which it is built. For we know from other sources the weight of individual atoms, and we know the total weight of the atoms in a cubic centimetre of the crystal. In this way we find that the nearest distance between two

atoms in rocksalt is $2 \cdot 81 \times 10^{-8}$ cm., which distance is also the spacing of the planes parallel to a cube face. From a knowledge of this quantity the length of any X-ray wave can be calculated at once as soon as the angle of its reflection by the cube face has been measured. In other words, the spectrometer has now become a means of measuring the length of waves of any X-radiation, and the actual spacings of the atoms of any crystal.

From this point the work branches out in several directions. It will not be possible to give more than one or two illustrations of the progress along each branch.

Let us first take up the most interesting and important question of the " characteristic " X-rays. It is known that every substance when bombarded by electrons of sufficiently high velocity emits X-rays of a quality characteristic of the substance. The interest of this comparison lies in the fact that it displays the most fundamental properties of the atom. The rays which each atom emits are characteristic of its very innermost structure. The physical conditions of the atoms of a substance and their chemical associations are largely matters of the exterior : but the X-rays come from the interior of the atoms, and give us information of an intimate kind. What we find is marked by all the simplicity we should expect to be associated with something so fundamental.

All the substances of atomic weight between about 30 and 120 give two strongly defined " lines " ; that is to say, there are found among the general heterogeneous radiation two intense almost homogeneous sets of waves. For instance, rhodium gives two pencils of wave-lengths, approximately equal to $0 \cdot 61 \times 10^{-8}$ cm. and $0 \cdot 54 \times 10^{-8}$ cm. respectively. More exactly the former of these is a close doublet having wave-lengths $0 \cdot 619 \times 10^{-8}$ and $0 \cdot 614 \times 10^{-8}$. The wave-lengths of palladium are nearly $0 \cdot 58 \times 10^{-8}$ and $0 \cdot 51 \times 10^{-8}$; nickel $1 \cdot 66 \times 10^{-8}$ and $1 \cdot 50 \times 10^{-8}$. Lately Moseley has made a comparative study of the spectra of the great majority of the known elements, and has shown that the two-line spectrum is characteristic of all the substances whose atomic weights range from that of aluminium, 27, to that of silver, 108. These X-rays constitute, there is no doubt whatever, the characteristic rays which Barkla long ago showed to be emitted by this series of substances.

Now comes a very interesting point. When Moseley sets the increasing atomic weights against the corresponding decreasing wave-lengths, the changes do not run exactly parallel with each other. But if the wave-lengths are compared with a series of natural numbers everything runs smoothly. In fact it is obvious that the steady decrease in the wave-length as we pass from atom to atom of the series in the periodic table implies that some fundamental element of atomic structure is altering by equal steps. There is excellent reason to believe that the change consists in successive additions of the unit electric charge to the nucleus of the atom. We are led to think of

the magnitude of the nucleus of any element as being simply proportional to the number indicating the place of the element in the periodic table, hydrogen having a nuclear change of one unit, helium two, and so on. The atomic weights of the successive elements do not increase in an orderly way ; they mount by steps of about two, but not very regularly, and sometimes they seem absolutely to get into the wrong order. For example, nickel has an atomic weight of 58·7, whereas certain chemical properties and still more its behaviour in experiments on radio-activity indicate that it should lie between cobalt (59) and copper (63·6). But the wave-lengths, which are now our means of comparison, diminish with absolute steadiness in the order cobalt, nickel, copper. Plainly, the atomic number is a more fundamental index of quality than the atomic weight.

It is very interesting to find, in the series arranged in this way, four, and only four, gaps which remain to be filled by elements yet undiscovered.

Let us now glance at another and most important side of the recent work, the determination of crystalline structure. We have already referred to the case of the rocksalt series, but we may look at it a little more closely in order to show the procedure of crystal analysis.

The reflection of a pencil of homogeneous rays by a set of crystalline planes occurs, as already said, at a series of angles regularly increasing ; giving, as we say, spectra of the first, second, third orders, and so on. When the planes are all exactly alike and equally spaced the intensities of the spectra decrease rapidly as we proceed to higher orders, according to a law not yet fully explained. This is, for example, the case with the three most important sets of planes of sylvine, those perpendicular to the cube edge, the face diagonal, and the cube diagonal respectively. An examination of the arrangement of the atoms in the simple cubical array of sylvine shows that for all these sets the planes are evenly spaced and similar to each other. It is to be remembered that the potassium atom and the chlorine atom are so nearly equal in weight that they may be considered effectively equal. In the case of rocksalt the same may be said of the first two sets of planes, but not of the third. The planes perpendicular to the cube diagonal are all equally spaced, but they are not all of equal effect. They contain alternately, chlorine atoms (atomic weight 35·5) only and sodium atoms (atomic weight 23) only. The effect of this irregularity on the intensities of the spectra of different orders is to enhance the second, fourth, and so on in comparison with the first, third, and fifth. The analogous effect in the case of light is given by a grating in which the lines are alternately light and heavy. A grating specially ruled for us at the National Physical Laboratory shows this effect very well. This difference between rocksalt and sylvine and its explanation in this way constituted an important link in W. Lawrence Bragg's argument as to their structure.

When, therefore, we are observing the reflections in the different faces of a crystal in order to obtain data for the determination of its structure, we have more than the values of the angles of reflection to help us : we have also variations of the relative intensities of the spectra. In the case just described we have an example of the effect produced by want of similarity between the planes, which are, however, uniformly spaced.

In the diamond, on the other hand, we have an example of an effect due to a peculiar arrangement of planes which are otherwise similar. The diamond crystallizes in the form of a tetrahedron. When any of the four faces of such a figure is used to reflect X-rays, it is found that the second order spectrum is missing. The analogous optical effect can be obtained by ruling a grating so that, as compared with a regular grating of the usual kind, the first and second, fifth and sixth, ninth and tenth alone are drawn. To put it another way, two are drawn, two left out, two drawn, two left out, and so on. The National Physical Laboratory has ruled a special grating of this kind also for us, and the effect is obvious. The corresponding inference in the case of the diamond is that the planes parallel to any tetrahedral face are spaced in the same way as the lines of the grating. Every plane is three times as far from its neighbour on one side as from its neighbour on the other. There is only one way to arrange the carbon atoms of the crystal so that this may be true. Every atom is at the centre of a regular tetrahedron composed of its four nearest neighbours, an arrangement best realized by the aid of a model. It is a beautifully simple and uniform arrangement, and it is no matter of surprise that the symmetry of the diamond is of so high an order. Perhaps we may see also, in the perfect symmetry and consequent effectiveness of the forces which bind each atom to its place, an explanation of the hardness of the crystal.

Here, then, we have an example of the way in which peculiarities of spacing can be detected. There are other crystals in which want of uniformity both in the spacings and in the effective value of the planes combine to give cases still more complicated. Of these are iron pyrites, calcite, quartz, and many others. It would take too long to explain in detail the method by which the structures of a large number of crystals have already been determined. Yet the work done already is only a fragment of the whole, and it will take no doubt many years, even though our methods improve as we go on, before the structures of the most complicated crystals are satisfactorily determined.

On this side, then, we see the beginning of a new crystallography which, though it draws freely on the knowledge of the old, yet builds on a firmer foundation since it concerns itself with the actual arrangement of the atoms rather than the outward form of the crystal itself. We can compare with the internal arrangements we have now discovered the external forms which crystals assume in growth, and the

modes in which they tend to come apart under the action of solvents and other agents. By showing how atoms arrange and disarrange themselves under innumerable variations of circumstances we must gain knowledge of the nature and play of the forces that bind the atoms together.

There is yet a third direction in which enquiry may be made, though as yet we are only at the beginning of it. In the section just considered we have thought of the atoms as at rest. But they are actually in motion, and the position of an atom to which we have referred so frequently must be an average position about which it is in constant movement. Since the atoms are never exactly in their places, the precision of the joint action on which the reflection effect depends suffers materially. The effect is greater the higher the order of the spectrum. When the crystal under examination is contained within a suitable electric furnace and the atoms vibrate more violently through the rise of temperature, the intensities of all orders diminish, but those of higher order much more than those of lower. The effect was foreseen by the Dutch physicist Debije, and the amount of it was actually calculated by him on certain assumptions. I have found experimental results in general accord with his formula. In passing it may be mentioned that as the crystal expands with rise of temperature the spacing between the planes increases and the angles of reflection diminish, an effect readily observed in practice.

This part of the work gives information respecting the movements of the atoms from their places, the preceding respecting their average positions. It is sure, like the other, to be of much assistance in the enquiry as to atomic and molecular forces, and as to the degree to which thermal energy is locked up in the atomic motions.

This brief sketch of the progress of the new science in certain directions is all that is possible in the short time of a single lecture : but it may serve to give some idea of its fascination and possibilities.

[W. H. B.]

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Problems of Hydrogen and the Rare Gases.

IN the course of the Friday Evening Discourse of last year on " The
Coming of Age of the Vacuum Flask " attention was drawn to some
low temperature determinations of the amount and distribution of
hydrogen, helium and neon in gases from various sources. This work
has now been extended by the use of improved apparatus and methods
of manipulation. To measure with accuracy the presence of a few
parts per million of one or other gases, either by volume or weight,
diluted to such a large proportion in another, is not an easy problem.
What a millionth part represents is shown in the model on the table.
The framework encloses a cubicle space one metre in the side, in the
centre of which a cube of one centimetre in the side is suspended.
The relative volumes of these cubes are as 1 to 1,000,000. When it
is stated that the air contains less than one part in a million of
hydrogen, this means less than one cubic centimetre per cubic metre.
The values given last year were derived from measurements of the
partial pressure observed in a McLeod gauge, after the gases had
been cooled to 20° Abs. by the use of liquid hydrogen from an initial
pressure of 760 mm., or one atmosphere. The unit of pressure
adopted to express the recorded results was 10^{-4} $(\frac{1}{10000})$ mm.
mercury pressure, and that mode of expressing the experimental
results will be continued in this lecture.

COMPARATIVE CONDENSABILITY OF GASES BY CHARCOAL AT LIQUID AIR AND LIQUID HYDROGEN TEMPERATURES.

The relative condensability by charcoal of the gases, air, hydrogen,
and helium, can be shown by filling three similar sets of double
tubes with samples of these gases. The two tubes of each set are
filled with the particular gas at atmospheric pressure and the
ordinary temperature, and dip into a little bottle of mercury. The
tubes are bent twice at right angles and sealed up. Thus the closed
end of either tube of each set can be cooled by immersion in a

vacuum vessel containing liquid air or hydrogen. A gramme of charcoal is placed in the sealed end of one tube in each pair. For convenience of pressure observations, a barometric tube is placed alongside each pair of tubes in the three separate little bottles of mercury.

When the closed end of the air tube is cooled in liquid air, only a small contraction is observed, as shown by a slight rise of the mercury in the tube. If, however, the air tube which contains the charcoal is cooled all the air is thereby condensed, and the mercury quickly rises to the barometric height. Now take the pair of hydrogen tubes. As before, on cooling the tube without charcoal, only a slight contraction is shown, but when the charcoal tube is immersed in the liquid air, a quantity of the hydrogen is condensed in the charcoal, and the mercury rises in the tube. The height the mercury attains, however, is noticeably less than in the air-charcoal tube, showing the smaller condensability of hydrogen in the charcoal at liquid air temperature. When either of the helium tubes are cooled with liquid air, practically no condensation is shown.

Now instead of liquid air, let us use liquid hydrogen, and cool first the air tube. Immediately the mercury rushes up to the barometric height, all the air being condensed into a solid of inappreciable tension of vapour, and the charcoal tube behaves in the same way. Now pass to the hydrogen tubes. When the plain gas tube is cooled, quite a noticeable contraction is visible, because the temperature of liquid hydrogen is so low compared to hydrogen gas at the room temperature. Complete absorption is produced when the charcoal-hydrogen tube is cooled and the mercury rises to the barometric height. The hydrogen, at the temperature of its own boiling point, is completely absorbed in the charcoal.

Now compare this with the set containing helium. The helium tube when cooled behaves similarly to the plain hydrogen tube, but on cooling the charcoal tube, quite a large diminution of pressure is produced, showing that even helium is condensed to a considerable extent by charcoal at 20° absolute. As the charcoals warm up, the condensed gases are again expelled ; the helium very rapidly, the hydrogen somewhat more slowly, and the air after some few minutes.

APPARATUS EMPLOYED FOR MEASUREMENTS OF HYDROGEN AND THE RARE GASES UNCONDENSED AT THE BOILING POINT OF HYDROGEN. (Plate 1.)

In order to avoid indiarubber connections, vitiating the accuracy of the values of minute quantities of gas, the gas to be examined was contained in a flask A of suitable size, attached by a coned ground joint T. The gas was allowed to enter the exhausted apparatus by opening the cock B, which also served to connect to the pump for the preliminary exhausting of the whole apparatus. To remove hydrogen and hydrocarbons the part between B and the measuring burette C

contained a roll of oxidised copper gauze tightly filling about 8 cm. of the centre of the tube. For safely heating this a thin tube of iron about 5 mm. greater in diameter was secured in position by asbestos wool packed in at the ends. A bent sheet of asbestos served
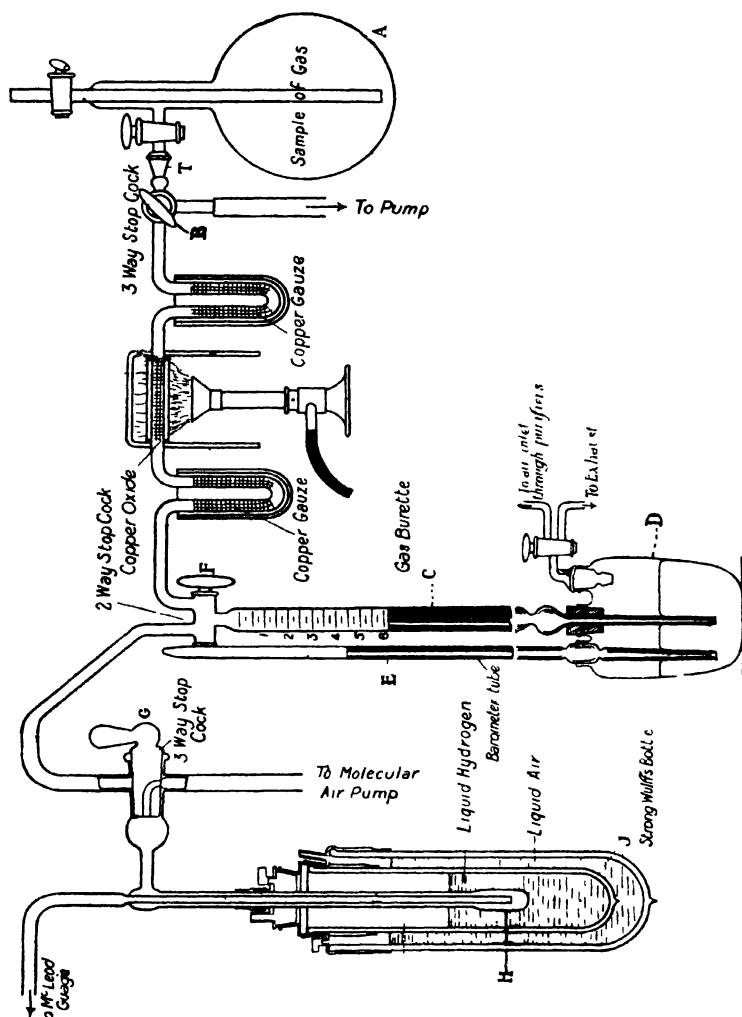
PLATE 1.

to further unify the heating, which was supplied by a small fan-shaped bunsen flame, just not luminous. On either side of the oxidised copper the tube is bent into a U shape for cooling in liquid air, to condense any volatile hydrocarbons from the stopcock and the oxidised products from the action of the hot CuO on any combustible material in the gas sample.

The exact measurement of samples small in volume is made by lowering the pressure to any convenient amount in the burette C, in which the gas collects during the purification by heated CuO. The burette opens below under the surface of mercury in a vessel D with a connection to the exhaust pump ; an exhausted tube E as barometer also opens into the mercury in the same vessel. From the difference of levels of the mercury in C and E the real volume of the gas sample at normal temperature and pressure can be determined. After measuring the gas, the cock F is turned to connect to the main stopcock G, by which the gas is cautiously admitted to the cooling bulb H, and through this to the McLeod gauge ; G also connects by another way to the molecular pump, by which the cooled products can be highly exhausted. The bulb H is formed of two concentric tubes $1\frac{1}{2}$ cm. and $\frac{1}{2}$ cm. diameter respectively. The inner tube is continued up to connect to the gauge, while the connection to G is on the annular space ; by this means no gas can reach the gauge until it has passed through the cooled part of the bulb H immersed in the liquid hydrogen.

When the charcoal and liquid air method is employed, 10 grams of charcoal are placed in an enlarged part of the tube H, which is immersed in the liquid hydrogen. Liquid air or liquid nitrogen or oxygen replaces the liquid hydrogen in the inner of the vacuum vessels J, the outer still containing liquid air, under exhaust if necessary.

The volume of the cooling bulb and McLeod gauge up to the main·stopcock G was carefully determined. The volume of the gas sample admitted through G being also measured, the ratio of this to the total volume of the gauge and cooling tube is known, from which the partial pressure which would result if the gauge had been filled with the gas at atmospheric pressure could be deduced.

This is given by observing the partial pressures with successive increasing volumes of gas occluded in the charcoal. Plate 2 expresses the results graphically. The partial pressures observed are ordinates, while the abscissæ are the gas volumes admitted. The two lowest graphs, Nos. 1 and 2, show the values given when 10 grams of charcoal at the respective temperatures of 77° Abs. (boiling liquid nitrogen) and 86° Abs. (old liquid air, temperature controlled by oxygen vapour tension thermometer) are employed as cooling agents. The volume of successive increments was 50 or 100 c.c. ; the volume of the apparatus was just over 350 c.c. ; therefore not until this volume had been admitted does the recorded partial pressure correspond to 760 mm., or one atmosphere, in the gauge. This

is therefore so marked on the diagram, and the ordinate at this point can be scaled in parts per million volumes, the unit for this scale being equal to $7 \cdot 6 \times 10^{\cdot}$ mm. mercury pressure, which is one millionth of an atmosphere. The rise of pressure is at first linear in both cases, but after the admission of 300 c.c. in the second case the graph begins to bend upwards, and the rate of this bending becomes greater with further increments, showing that the partial pressure of those constituents condensed by the charcoal, which up to now had been low, here begins to be appreciable as the concentration in the charcoal increases. The place at which this bending begins depends on the weight of charcoal employed and the mode in which it has been prepared. The two upper graphs, Nos. 3 and 4, are perfectly linear, which is characteristic of the
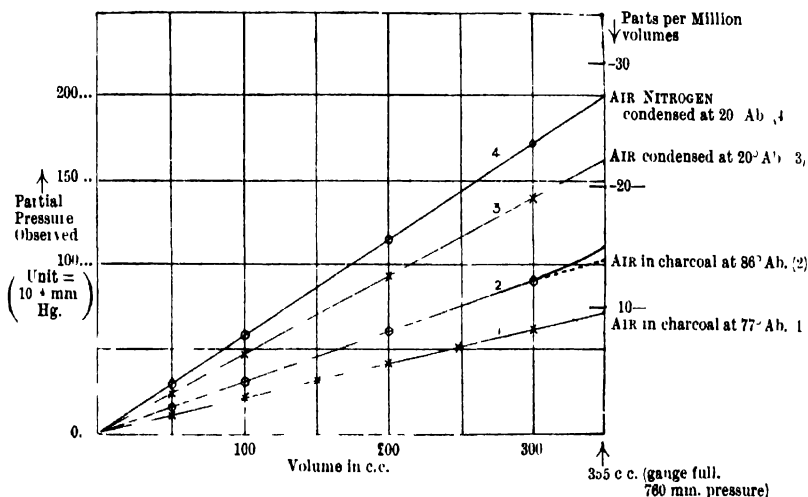
PLATE 2.—PROPORTIONS OF HELIUM AND HYDROGEN IN AIR.
Comparison of the Use of Charcoal at Liquid Air Temperature with that
of Liquid Hydrogen.

results obtained when liquid hydrogen is employed as condensing agent alone. No. 3 deals with ordinary air, and is thus comparable to the charcoal and liquid air results just discussed. No. 4 shows the values obtained when the oxygen is removed from the air, leaving only "air nitrogen." The uncondensable portion is now relatively higher in the same volume, which should be the case if it remains unaffected by the oxygen absorption.

The difference in the values recorded in No. 3 from those in Nos. 1 and 2 represents the amount of condensation of hydrogen and neon in the charcoal. This is confirmed by its being greater at the lower temperature of boiling nitrogen, No. 1, which lies below No. 2

obtained with liquid air, some 9 degrees higher. The approximation of No. 2 to No. 3 as the higher concentrations are reached is due to the rapidly increasing tension of neon and hydrogen in charcoal containing relatively large amounts of occluded nitrogen and oxygen. The disturbance in the equilibrium of the condensed constituents under these conditions is beginning to be appreciable. To illustrate the problems resulting from such a condition the following experiment is instructive : Two similar U-shaped bulbs charged with 10 grms. of charcoal and provided with inlet and outlet stopcocks are cooled in liquid air and opened to the atmosphere of the room. One is simply allowed to saturate itself from the air, while the second has a slow current of dry air passed through it for some time after saturation. This having been done, both bulbs are warmed up by immersion in tepid water, and the gases so expelled are roughly tested by inserting a glowing splint of cedar-wood ; the gas issuing from the first bulb at once extinguishes the splint, whereas that coming from the second excites a brilliant combustion. Nitrogen is given off from the bulb which has been saturated by atmospheric air ; whereas oxygen principally results after the air current to which the second charcoal was subjected. In the latter case the less volatile and more condensable oxygen has accumulated in the charcoal to a greater extent to that of nitrogen. The slow current of dry air has provided the opportunity for the equilibrium of the two gases occluded in the charcoal to be established ; but when air rushes in at atmospheric pressure, filling the pores of the charcoal in a small limited space, the proportions of each gas present in the charcoal must have substantially the composition of the ordinary air. Thus, on warming up each of these samples of charcoal which have been treated as above described, it is to be anticipated that the one sample of charcoal would give gas containing excessive nitrogen and the other excessive oxygen.

The alteration of the proportions of helium, neon and hydrogen in air when it has been equilibriated in charcoal at liquid air temperature is given in the following table : —

ALTERATION OF THE PROPORTIONS OF HELIUM, NEON AND HYDROGEN IN OCCLUDED AIR IN CHARCOAL AT LIQUID AIR TEMPERATURE. (Plate 3)

Material	Parts per Million Volumes	
	Helium and Neon	Hydrogen
City air	22·5	10·6
Country air	22 8	0·5
Gas occluded in charcoal after air current at 85° Abs.	1·64	6 1
Above repeated with compressed air from steel bottles	1·53	9·8

GAUTIER'S OBSERVATIONS OF 1901.

	Hydrogen
City air	200
Mountain air	170
Sea air	190

Charcoal has less condensing power for the rare gases than for nitrogen ; so that if the proportion of nitrogen in the charcoal gases after a long air current at 85° Abs. be lower than in ordinary air, we should expect the proportion of the rare gases to be still more greatly diminished. The values observed prove that this is so ; only 1·64 parts per million of the rare gases helium and neon being present, instead of the 22·5 parts in ordinary air, and the total of the helium, neon and hydrogen is only 7·7, instead of 25·1. Although the proportion of hydrogen is exceedingly small in air, yet it is quite appreciably condensed by charcoal at liquid air temperature, having been increased from 1·6 to 6·1 by such treatment. Its proportion has, in fact, been increased ten-fold, while that of the helium and neon has been reduced to one-fourteenth, due to the charcoal having practically little power of absorption for these gases at liquid air temperatures.

In a second experiment the air with which the charcoal was treated was taken from a steel bottle in which it had been first compressed : the amount of hydrogen in the evaporated product was then higher by one-half—9·8 instead of 6·1—although the neon and helium value was not sensibly different. The higher proportion of hydrogen is explicable by the chemical action of water on the iron storage receptacle. Gautier, in 1901, employed metallic tubing in his apparatus for measuring the amount of hydrogen present in air, with the result that he obtained a value as high as 200 parts per million with city air, the lowest amount being 170 in mountain air. This must have arisen from the chemical action on the metallic tubing producing hydrogen. On the subject of the relative distribution of the atmospheric rare gases in thermal springs and air, Moureu, in 1913, found that the ratio of any two of the gases present in air to the same pair in the gas from thermal springs is roughly constant except where helium is concerned. The table on the following page epitomises his results. Krypton and xenon, as well as the more common argon, are less volatile than the ordinary atmospheric gases oxygen and nitrogen, whereas helium is the most volatile known gas.

MOUREU'S EXPERIMENTS (1913).
COMPARISON OF DISTRIBUTION OF RARE GASES IN AIR AND IN
EARTH GASES.

Gases from Thermal Springs and Fire Damp		Air	Ratio
$\dfrac{\text{Krypton}}{\text{Argon}}$	divided by	$\dfrac{\text{Krypton}}{\text{Argon}}$	Roughly constant
$\dfrac{\text{Xenon}}{\text{Argon}}$	,,	$\dfrac{\text{Xenon}}{\text{Argon}}$	,,
$\dfrac{\text{Xenon}}{\text{Krypton}}$	,,	$\dfrac{\text{Xenon}}{\text{Krypton}}$	,,
$\dfrac{\text{Helium}}{\text{Argon}}$	,,	$\dfrac{\text{Helium}}{\text{Argon}}$	Varies enormously

The measures of such small quantities of gas, as are here being discussed, will, of course, be liable to errors from many causes, and the conditions of experimenting must therefore be modified in the search for possible variations. For this purpose the application of a high exhaust, such as that obtained by the use of the molecular pump, in conjunction with the cooling methods already described, has yielded some suggestive information.

The manner in which such experiments can be carried out can be seen by referring back to Plate 1. The main stopcock B on the cooling bulb H there shown, besides the connection to the burette, can be turned on to the high exhaust of the molecular pump. By this means both the condensed products in the bulb H and the uncondensable residue in the gauge are subjected to an exhaust of below 0·00001 mm.; which is one-tenth of the unit of pressure employed to express the results; and approximately one two-thousandth part of the partial pressure in the gauge of the uncondensable fraction in air. The readings then obtained are shown in the next table :—

PLATE 4.—OCCLUSION AT 20° ABS. OF THE UNCONDENSABLE FROM AIR
IN THE CONDENSED SOLID NITROGEN AND OXYGEN

Material used	Partial Pressures (in 10⁻⁶ mm) left from 760 mm		
	Cooling to 20° Abs.	Exhaust of Molecular Pump for 10 min. at 20° Abs.	Raised to 15° C., Recondensed at 20° Abs
			(Amounts occluded)
Air	181	0·11	4 6
Air nitrogen . .	218	0 075 (1) 0·08 (2) 0·075 (3) 0·07 (4)	1·5 (1) 0·31 (2) 0·10 (3) 0·11 (4)

Air and air nitrogen were the materials examined, as stated in the first column. As oxygen is absent in the second case, some idea of the effect of its presence can thus be obtained. The second column gives the partial pressure of the residue of rare gases uncondensed at 20° Abs. The next column shows the reduced pressure in the apparatus when the exhaust pump was connected, and continued in action for over 10 minutes, the uncondensable residue being thereby removed down to the limit which the pump can maintain under the circumstances. The exhaust was then closed off, and the condensed material allowed to evaporate off into the apparatus, by lowering the liquid hydrogen vessel away from the bulb H until everything was at room temperature. The bulb was then again cooled by cautiously and slowly raising the vessel of liquid hydrogen to its former position ; the steady pressure then obtained is recorded in the last column. This value is seen to be higher than that left by the pump exhaust. By repeating the operation a state can be reached when only a very small increase is registered, as shown when the air nitrogen was examined.

This means that even at the low pressure maintained by the pump some helium or neon or hydrogen has been held bound, or dissolved in the solid condensed nitrogen and oxygen ; so that the value obtained by simple condensation to 20° Abs. is low by at least this amount, though no doubt the amount of occlusion at the higher initial observed pressure of the uncondensable is even greater than that at the lower pressure of the pump ; the nature of this occluded material remains to be seen. Having regard to the relative volatility of hydrogen, neon and helium, one might expect that hydrogen would most likely be present in any gas remaining occluded under high exhaust in solid nitrogen and oxygen at 20° Abs. Experiment, however, seems to suggest that the very opposite is the case. To examine this question, mixtures of hydrogen with nitrogen and carbonic oxide respectively were employed ; the table on the following page gives the results.

The first column shows the gases used in the experiments. In the second column is given the partial pressure of each constituent after admission to bulb H and the McLeod gauge of Plate 1. Following this is recorded the actual pressure registered on cooling the bulb H in liquid hydrogen ; and in the next column the apparent occlusion before exhausting, being the difference between the partial pressure of the hydrogen in the case of the mixtures shown in column 2 and the reading of column 3, which is the pressure observed. At this point, following the former procedure, the molecular pump exhaust was connected for 15 minutes ; then, as before, the condensed material remaining was evaporated off into the gauge by removing the liquid hydrogen. But before re-cooling to determine any uncondensable residue due to occlusion at the high exhaust, which would be a completion of the previous experiment, a

PLATE 5.—EFFECT OF PRESENCE OF HYDROGEN ON THE VOLATILITY
AT 20° ABS. OF NITROGEN AND CARBONIC OXIDE.

Gas and Gas Mixtures Examined	Pressure (in 10 ⁴ mm.)			
	Gas at 15° C.	Cooling to 20° Abs.	Apparent Occlusion (before Exhaust)	Raised to 15° C after 10 min High Exhaust at 20° Abs.
Air nitrogen	16920 (0·82 c.c.)	0·47	—	{ 16920 (all left)
Carbonic oxide .	28900 (1·89 c.c.)	40 (0·14% hydrogen)	—	{ 28570 (99° left)
{ Nitrogen, 20% { Hydrogen, 80%	5190 (0·25 c.c.) 20760 (1·00 c.c.)	16440	{ 4320 (16·7%)	0·44 (i e. none left)
{ Carbonic Oxide, 20% { Hydrogen, 80%	2390 (0·116 c.c.) 9560 (0·464 c.c.)	7600	{ 1960 (9·7%)	0·12 (i.e. none left)

measure of the pressure was taken to determine the amount of the
evaporated material obtained, with the surprising result, in the case of
the hydrogen mixtures, that there was nothing practically to measure.
Under the high exhaust of the pump, therefore, not only had the
uncondensable hydrogen been removed, but also the condensable
constituent; nitrogen, or carbonic oxide, had suffered a forced vola-
tility in presence of the hydrogen, although naturally without
admixture of hydrogen, the nitrogen or carbonic oxide was regained
unaltered.   In view of this, it seems difficult to resist the conclusion
that some sort of molecular aggregation had taken place at the very
low temperature, between hydrogen and the carbonic oxide and
nitrogen respectively.

The composition of the gases in this experiment is of course very
different from that dealt with in determining the small proportion of
air uncondensable.   There is, therefore, only a limited application to
that case.   Thus the amount of condensed nitrogen employed is only
one-fourth of the total amount of hydrogen, whereas in the experiment
with ordinary air there is five hundred thousand times more nitrogen
than hydrogen; the amount of "forced volatility" will therefore
probably be so small as to escape measurement, as the difference to
be detected would have to be measured on a total of one atmosphere
in the gauge.   Further, it is possible to make a correct estimate of
the amount of occlusion occurring on condensation to 20° Abs. in
the case shown in the last table, because the actual composition of

the mixture is known ; whereas in the former case of examination of air uncondensable, this is uncertain, the only data being the pressure remaining after exhaust and recondensation. But there is evidently ample need for enquiry under different intermediate conditions in order to throw more light on what appear to be new conditions of relative volatility at low temperatures.

DIFFUSION THROUGH PLATINUM AND OTHER METALS AT HIGH TEMPERATURES.

The diffusion of hydrogen through a heated platinum tube can easily be demonstrated. For this purpose a platinum tube A (Plate 6) of $\frac{1}{2}$ mm. bore and $\frac{1}{2}$ mm. thickness of wall is fused up at
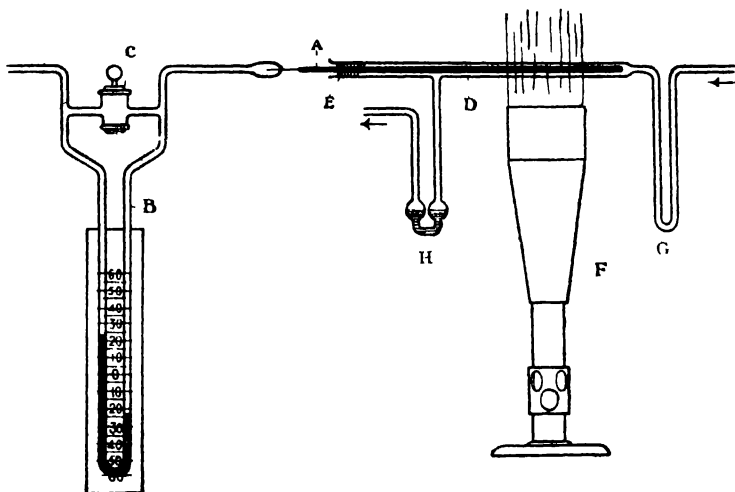
PLATE 6.

one end, while the open end is sealed into one limb of a glass manometer B charged with sulphuric acid ; the platinum tube is reduced to about 0·2 mm. thickness of wall for sealing into the glass. It is further supported by an external glass tube (not shown in the figure) fitting tight on to the horizontal extension of the manometer, and drawn out to afford a good sliding fit on about 5 cm. of the platinum tube. The left-hand limb of the manometer connects to a stopcock and charcoal bulb for exhausting between successive measurements ; to facilitate this, the two limbs of the manometer are connected by another stopcock C, which is closed when a measure is to be made. For providing atmospheres of different gases round the platinum tube, a quartz tube D of special

shape is slipped over the platinum tube, which it loosely fits, and to which it is luted at the plain open end nearest the sealed joint by a short plug of asbestos wool tightly packed when wet. The purification of the gas entering the quartz tube, and thus passing through the annular space round the platinum tube, is provided for by a plain U-bend G, which is cooled in a vessel of liquid air or solid carbonic acid. A second bulbed U-tube containing a little mercury or sulphuric acid is sealed in near the open end of the quartz cover tube, and this acts as a seal and bubbler H for controlling the gas rate. The tubes are conveniently heated by a Méker burner F.

Plate 7 shows the observed increase in the pressure when the platinum tube is heated directly in the flame in three different
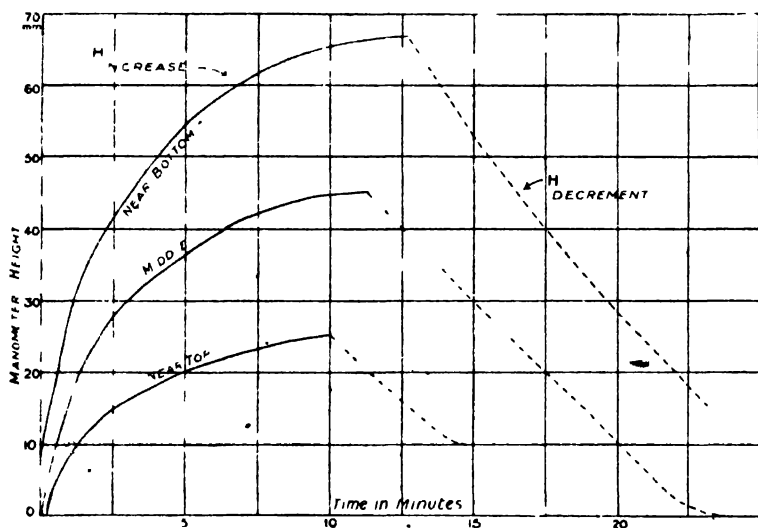
PLATE 7.—GROWTH OF PRESSURES IN PLATINUM TUBE HEATED BY MÉKER GAS BURNER.

positions. The rate of growth of the pressure and the limiting pressure reached are seen to be dependent on the region of the flame to which the platinum tube is adjusted; when near the bottom, where the amount of unburnt hydrogen is greatest, a rapid rise is shown and the equilibrium pressure obtained is high, both values becoming less as the platinum tube is brought higher in the flame. Finally, at the tip of the flame where combustion is complete, reversal can be demonstrated, and the manometer again falls in the manner shown in the diagram; for the hydrogen will diffuse out as well as in, the direction depending on whether the region of lowest pressure is outside or inside. The position of equilibrium of the

manometer, given by any part of the flame, records the partial pressure of the diffusing hydrogen for that region; this is easily shown in the middle of the flame. In the same way a pure hydrogen flame can be employed. The temperature of the flame is now not so high, but can be increased by the introduction of a little oxygen, using a simple form of quartz blowpipe. The oxygen introduced passes through an annular tube round the hydrogen jet, whereby the temperature of the tube is sufficiently raised by conduction from the outside intense part of the flame, while leaving plenty of available free hydrogen to diffuse from the central part. The manometer rises then to almost any amount we please. An actual rate of this diffusion has been measured by observing the growth of pressure in an exhausted McLeod gauge of known volume to which the platinum tube and attached U-tube was sealed. With the platinum near a white heat the rate was found to be of the order of 3 c.c. an hour per square centimetre through a mean thickness of half a mm. When thin platinum foil was employed in a different arrangement about twenty times this rate was observed at a rather lower temperature.

If instead of the flame impinging directly on the platinum tube we introduce the quartz tube cover shown in Plate 6, allowing dry air or oxygen to pass through the annular space, the manometer remains steady, whereas, however, on passing a current of hydrogen through the annular space the pressure instantly increases and quickly reaches a limit.

On replacing the platinum tube by a palladium one, similar effects result, but at a greater rate. Now, however, the pressure disappears when the flame is removed, as the palladium on cooling absorbs the hydrogen; but not so fast as when the tip of the flame is used for heating to show the diffusion of the hydrogen out through the hot tube. An iron tube similarly employed shows much smaller effects; but on the other hand this is the only tube of the three to give any indications of gas diffusion when heated by a flame of carbonic oxide raised in temperature by the addition of oxygen.

An even more effective and ready way to demonstrate a succession of these effects is by using an electric discharge tube to replace the manometer; the arrangement of the apparatus is seen in the next figure (Plate 8).

The platinum tube in this case is also provided when necessary with an external quartz tube for leading different gases over the heated platinum. For examining the electrical discharge and spectrum of the diffusing gases, the discharge tube B is provided with external electrodes, formed by silvering 3 cm. length near each end, protected by thin copper foil bound on w th wire. Exhaust is provided as usual by a charcoal bulb C with a stopcock F for putting the exhaust off and on as required. B is protected at each end with U-tubes D and E, as liquid air traps for volatile materials, either

diffusing in or coming from the stopcock. The volume is kept small by using tubing of about 2 mm. bore. By this means the diffused pressure attains in a very short time a sufficient value to allow a discharge to pass.
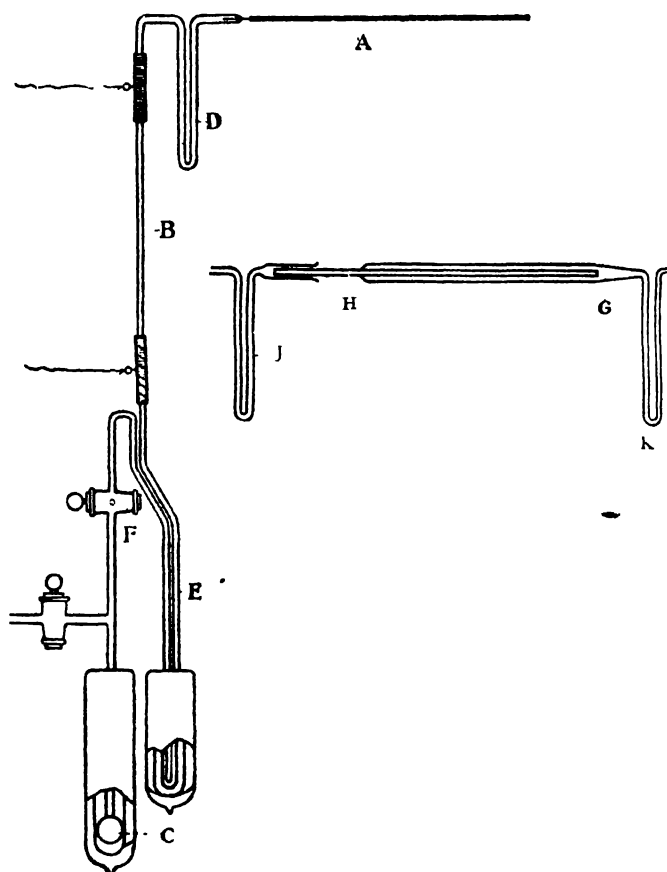
PLATE 8.

The apparatus being highly exhausted, as shown by the absence of any discharge when the induction coil is put on, the naked flame of the Méker burner is applied to the platinum tube. Within a very few seconds of closing off the charcoal stopcock a lilac-coloured discharge

begins in the tube and rapidly intensifies and becomes deep pink, characteristic of hydrogen, and on examining with the spectroscope a well-developed spectrum of this gas is seen. Now the heating is repeated, after exhausting by the charcoal, but with the quartz tube containing air covering the platinum tube. This time no discharge will pass even after several minutes of heating as before. Other gases can then be passed through the annular space between the quartz tube and the platinum. Neither oxygen nor carbonic acid will show any diffusion under such circumstances, although at a somewhat higher temperature, obtained in some cases by passing a strong electric current through the platinum tube instead of using flame temperatures, there are indications that both carbonic acid and water vapour will pass through, and possibly also carbonic oxide, a gas which, as we have seen, readily passes through hot iron. Finally, when hydrogen is passed through the quartz tube a strong discharge is rapidly obtained.

If a thoroughly cleaned quartz tube is subjected to direct heating by the Méker flame, there is no certain indication of any gas transference. If the quartz tube, however, is attached to a McLeod gauge, instead of to the electric discharge tube, and the heating continued for a considerable time, then a definite increase of pressure can be detected. On the addition of the external quartz tube, as was done with the platinum tube, the arrangement can be made more convenient, as the two quartz tubes can be sealed together to form a double tube in one piece, as shown in Fig. 5. This arrangement further enables the annular space between the tubes to be well exhausted or filled to any required pressure with different gases. If hydrogen be admitted and the tubes strongly heated, a discharge can only be obtained after a long time, the rate of diffusion being very slow.

When helium and neon replace the hydrogen in the annular space, then a discharge is readily obtained. The helium appears more quickly than the neon, the discharge being sky-blue at first and steadily modifying to the well-known peach-blossom tint of helium and neon mixtures, and becoming a brilliant orange-pink as the neon intensifies. This affords an effective and ready manner of demonstrating the transference of these gases through hot quartz. The annular space was filled to about four-fifths of an atmosphere at ordinary temperature ; a good Méker flame is a sufficient source of heat ; the inner quartz tube is approximately $\frac{1}{2}$ mm. thick in the walls and about $1\frac{1}{2}$ mm. bore. To prevent much loss by diffusion into the air through the outer tube the quartz tube ought to be thick in the wall. After charging the annular space the helium and neon gasholder is sealed off. The measure of the rate of transference of helium and neon by the use of a McLeod gauge has not yet been made.

DIFFUSION THROUGH INDIARUBBER.

A widely different example of a diffusing medium is afforded by indiarubber stretched into thin membranes. To enable them to stand the necessary difference of pressure on the two sides they are supported on discs of copper gauze mounted in a shallow metal drum of about 4 cm. diameter ; the drum A, Plate 9, is closed at one end by a brass plate pierced to connect to a lead tube E, of about 2 mm. bore and 8 mm. diameter. Connection is made to the manometer by a ground coned joint B ; a brass cone fitting this joint is soldered on the end of the lead tube. The indiarubber membrane is stretched
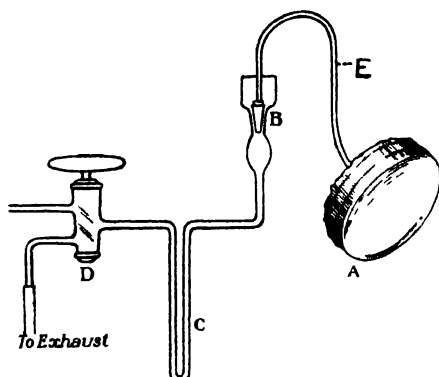
PLATE 9

over the open end of the drum and rests on the copper gauze disc inside, which is raised a few millimetres above the brass plate forming the closed end of the drum. Tightly wound thread is used to bind on the membrane, a little melted indiarubber as luting being first smeared thinly on the brass. To enable different gases to be used, and their temperature and pressure to be varied, as applied to the indiarubber membrane, a gas-tight metal box is fitted on (this is not shown in the diagram).

For demonstrating diffusion through the membrane a manometer is employed of the same pattern as that shown in Plate 6 ; the index tube is charged with very high boiling-point mineral oil instead of sulphuric acid. In order to dry or purify the diffusing gas a plain U-tube C (Plate 9) is sealed to the coned joint connecting to the mounted membrane. Beyond the U-tube is a two-way stopcock D, whose upper limb is sealed to the manometer, while the lower

connects to an exhaust pump for the preliminary exhaust of the space between D and the indiarubber.

Everything being exhausted, the U-tube C is cooled in liquid air, while the ordinary air of the room is present in the gas-box round the indiarubber. In half-a-minute a difference of pressure of over 10 mm. is registered on the manometer. This, then, represents the rate due to pure dry air diffusing in through the membrane and through the cooled U-tube to the manometer.

If C is not cooled, and A is simply surrounded with a beaker lined with wet paper, then a pressure of 30–40 mm. in half-a-minute is seen, the difference being due to the added rate of the aqueous vapour Other vapours can be similarly tried by dropping a small quantity of different liquids into beakers placed in turn round the mounted membrane. Thus with ether, chloroform and ammonia the manometer gives exceedingly rapid indications, about 5 cm. or more being registered in a few seconds. Less active vapours are benzene, alcohol, pyridine and acetonitrile. These are a few illustrations of what is no doubt a large field for future enquiry. A viscous liquid like glycerin stops all diffusion when painted on a dry film. The solution, however, in glycerin of substances such as chloroform, etc., causes the manometer to act immediately.

An interesting variation applicable to the subject of the discourse is the passage over the membrane of respired air dried through a tube in boiling solid carbonic acid ($-80°$ C.). The 5 per cent or so of carbonic acid therein contained gives an appreciable addition to the rise of the manometer shown by dry air alone. If the breath be "held" for a half-minute or so before expiring, the difference is accentuated. When dry oxygen, hydrogen, and carbonic acid respectively are passed through the box over the membrane, the corresponding pressures recorded are 10, 40, and over 100 mm. respectively in the half-minute. Hydrogen therefore goes through, roughly, at four times the rate of air, and carbonic acid at least ten times as fast.

More careful measures made with a McLeod gauge showed that for the same membrane the rate expressed in c.c. per day through each square centimetre at the ordinary temperature was $2·12$ for air, $8 4$ for hydrogen, and $30·0$ for carbonic acid. Different films give different values within certain limits, according to their condition and thickness, which last is of the order of $0·01$ mm. The rate of diffusion at different temperatures is readily determined by immersing the gas-box containing the indiarubber membrane in a fluid the temperature of which can be properly regulated. The variation of rate with temperature is found to be logarithmic, with a definite break in the curve at $0°$ C., and also at other points below this in the case of hydrogen and carbonic oxide; as far as experiments have been carried out. Helium has a slightly greater rate than air, while carbonic oxide and nitrogen are not far removed. Some of these

curves intersect at lower temperatures. When the indiarubber membrane is immersed in liquid air, the diffusion is too small to be seen on the oil manometer ; the actual rate as determined on the McLeod gauge being only about 0 002 or 0·003 c.c. per day through each square centimetre. These observations all refer to a difference of pressure of one atmosphere on the two sides of the membrane. The discussion of the results got by the action of varying pressures and temperatures must be deferred to a future occasion.[1]

[J D.]

Mr. W. J. Green, B.Sc., of the Davy Faraday Laboratory, has given valuable assistance in the conduct of the Investigation ; and Mr. J. W. Heath, F.C.S., in the Lecture arrangements.

Appendix to Lecture of Jan. 22, 1915

RECORDS OF EXPERIMENTS OMITTED FROM THE

LECTURE ON "PROBLEMS OF HYDROGEN AND THE RARE GASES."

Friday, January 22, 1915.

The behaviour of hydrogen and the Rare Gases in their passage through metals and other permeable materials have stimulated further investigation, since Graham published his classical researches in 1866. Some of the problems of gaseous transmission at high temperature through quartz, platinum and various metals were discussed in the Discourse of last year.*

TRANSMISSION THROUGH INDIARUBBER.

In the method adopted by Graham "a thin film of rubber from a small balloon" was stretched over "a thin plate of stucco" closing the upper end of a glass tube 1 metre in length, filled and inverted in mercury to give a Torricellian vacuum. Over this tube he fixed a "hood of vulcanised rubber, provided with a small entrance and exit tube" whereby different gases were introduced over the rubber, and their rate of transference into the vacuous space was determined. The values of the relative rates determined by Graham were as follows :—

Air	...	...	...	1 0	Oxygen	..	...	2·23
Nitrogen	...	...	0·87	Hydrogen	...	...	4·79
Carbonic Oxide	...	0 98	Carbonic Acid	...	11·83

The absolute rate of air at three different temperatures, through a thin coat of indiarubber on silk, were also given. Expressed in c.c. per day through each square cm. of membrane surface, the values are :

| Tempr. 0˚ C. | | 4 | 14 | 60 |
| Rate | ... | ... | 0·07 | 0·28 | 0·83 |

Wroblewski† in 1876 examined the diffusion of gases through absorptive substances. In the use of caoutchouc he found that a membrane 0·034 mm. thick was almost completely impervious to air. Carbonic acid diffused through at a rate proportional to its pressure on the membrane, and independently of the pressure of air on the other side when this was free from carbonic acid. The connection between this result and Henry's Law of Absorption was pointed out. Hydrogen he found took 3·6 times as long to diffuse as an equal volume of carbonic acid ; and in a mixture of the two, each diffused independently at a rate proportional to its partial pressure.

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* Problems of Hydrogen and the Rare Gases. Proc. Roy. Inst., XXI., p. 543.
† Ann. Phys. Chem. 158, 1876, pp. 539-568; Rep. der. Physik. 12, 1876, pp. 423-453.

Apparatus for Study of Rubber Diffusion.

For the purpose of extending Graham's investigation, membranes about 0·01 mm. thick were used for demonstrating some aspects of the diffusion of gases and vapours. The thickness after use was determined by immersing the membrane in liquid air, mounted on its brass-drum support, thereby changing it into a rigid body that could be cut off at the low temperature and subsequently weighed ; knowing the specific gravity and the area the thickness is found.

Sheet Para rubber, about 1 mm. thick was gently warmed and carefully pulled in all directions by the hands, before being stretched on the brass support ; the outside edge being thinly coated with

(a)　　　　　　　　　　　　　　　(b)
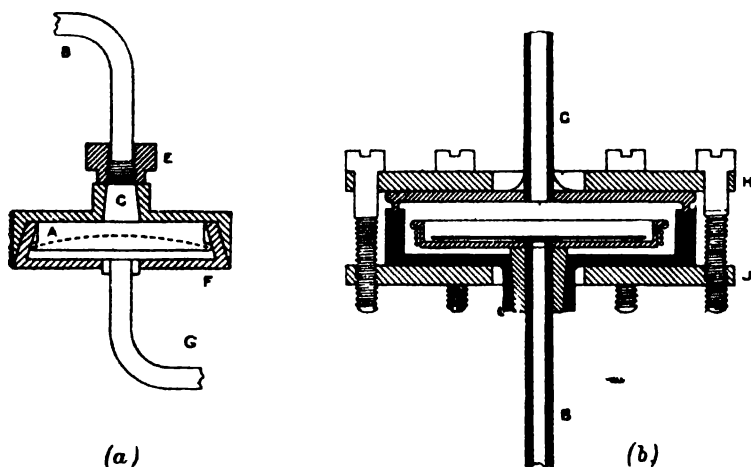
Fig. 16.

melted rubber. It was found most convenient for one person to stretch and hold the membrane down in position while a second person carefully wrapped and tied on the securing thread. Much thinner films could be obtained from the material employed by dentists, giving three times the percolation shown by the stretched Para, but they were often faulty through small leaks, and had to be abandoned.

For maintaining different conditions of temperature and pressure, the mounted membranes were enclosed in boxes which were gas-tight. The two types employed are shown in Fig. 16—

(a) for pressures at or below one atmosphere ;
(b) for pressures above one atmosphere.

In (a) the membrane is stretched across the open end of the shallow metal drum A. Just inside this a copper gauze disc is fixed to support the film against suction from within, communicated along the lead tube B, which connects by a ground joint to the highly

exhausted manometer* or McLeod gauge. A charcoal liquid air vacuum arrangement serves for conveniently producing and renewing the exhaust in the manometer ; but in the case of the McLeod gauge the molecular pump is more suitable. The tube B is soldered gas-tight into a coned and threaded boss C forming the centre of the closed end of A. The hollow brass cylinder D completely encloses A, on to the boss of which it fits tightly by its coned neck. A nut E secures the arrangement against subsequent differences of pressure. The rim of D is slightly coned inside to a similar hollow cylinder F, which thus completes a gas-tight box enclosing the membrane. A second lead tube G similar to B opens into F and leads to a two way stop-cock, whereby the box is exhausted and filled to the required pressure with the dried and purified gas to be examined. The tube G is bent in a half circle and brought up parallel to B, so that the whole arrangement can be enclosed in a bath at any required temperature. For the use of higher pressures the two halves of the gas box seen in (b) fit together with a spigot joint filled with a thin lead washer, and are securely bound by peripheral screws on the external ring-plates H and J. Five or six discs of coarse dried filter paper are placed under the indiarubber membrane and form a readily permeable support. The 2 mm. opening of B is covered by very fine mesh copper gauze under the filter paper. The drum supporting the membrane is only 2 or 3 mm. deep. This arrangement was tested to forty atmospheres pressure. The pressure was regulated by a screw valve attached to the bottles containing the compressed gases. The gas passing through the membrane under high pressure appeared as a slow stream of bubbles issuing from B, and could be collected and measured in the ordinary way. At low temperatures and pressures the gas transference was measured, in this case also, either by the increase of pressure shown on an exhausted U-tube manometer of known volume connected to B, or by a McLeod gauge when necessary.

The rates of diffusion measured at a pressure of one atmosphere with the apparatus of Fig. 1 gave the following values at 15° C. :—

	Relative Rates	Rate expressed in c c. per day per sq cm.
Air	1·0	2·0
Nitrogen	0·69	1·38
Carbonic Oxide	0·94	1 88
Helium	1·75	3·5
Argon	1·28	2·56
Oxygen	2·0	4·0
Hydrogen	5·6	11 2
Carbonic Acid	14 0	28·0

* See Fig. 9 : Problems of Hydrogen and the Rare Gases. Proc. Roy. Inst. XXI., p. 558.

The relative rates of diffusion given in the table between the different gases is not preserved at all temperatures   Thus at 0° C. carbonic acid has 16 times the rate of air, instead of 14 as given above for 15° C. In another case one film at 2° C. gave 1, 4 and 1·65 for the relative rates of air, hydrogen and helium.   Further, the absolute rates, given
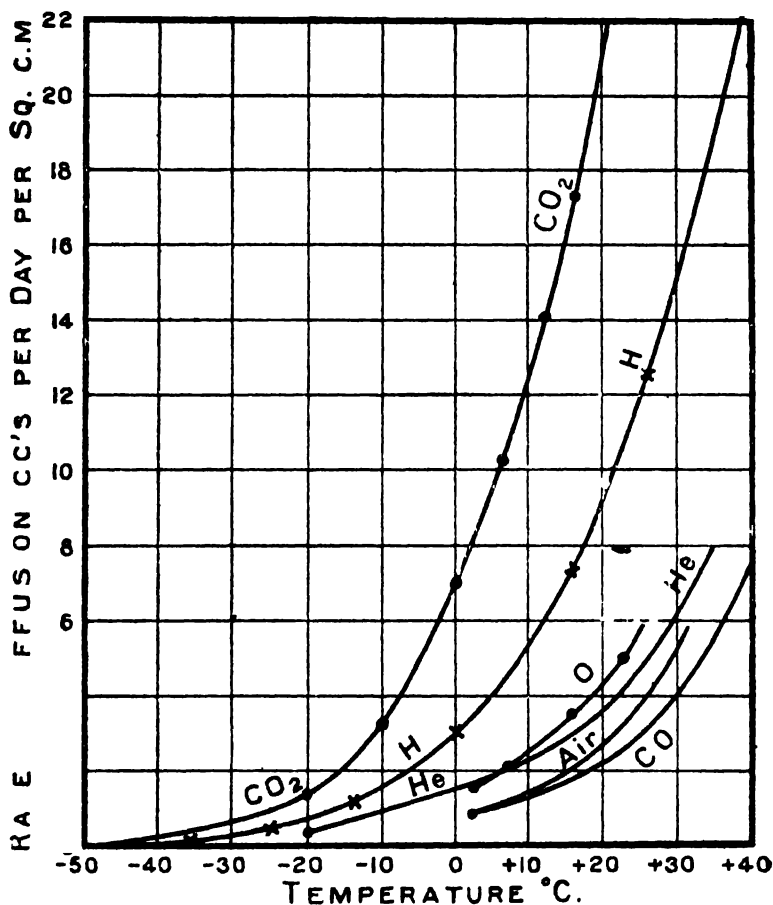
Fig. 17.

in the second column, are mean values, the films differing slightly in thickness.   Extreme variations obtained were 1·2 and 3·2.

The order of diffusibility shown in the above table is difficult to associate with any chemical or physical property of the gases concerned.   Especially is this the case with helium, the most volatile of

all gases, having an atomic weight of 4, which is only one-eleventh of the weight of the carbonic acid molecule, whose rate of diffusion is nevertheless eight times that of the lighter helium. Also the relatively slow rate of helium compared to hydrogen is remarkable in view of the diffusion of these gases through quartz, in which case helium has much the greater rate.
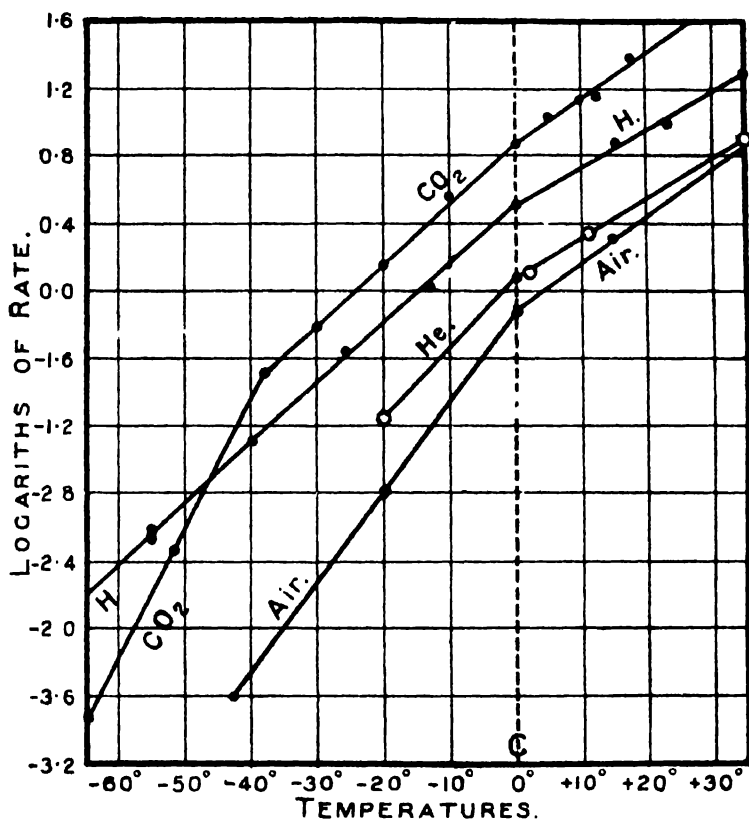
FIG. 18.

RELATION OF TEMPERATURE TO RATE OF GAS DIFFUSION THROUGH INDIARUBBER.

Fig. 17 gives the curves, showing the observed variation of the rate of gas transference with temperature in the case of six typical gases. In Fig. 18 the logarithms of the rates are plotted vertically, instead of the actual rates, with temperature horizontally

as before ; and in every case straight line graphs are thus obtained.
These straight lines all show a marked deviation at 0° C., which
naturally suggests that water in some condition is the associated
cause.   In the case of carbonic acid, another break was obtained at
about – 37° C.   The gases used were dried through a suitably cooled
U-tube before entering the box round the membrane shown in
Fig. 1 (a) ; but there is the possibility that water in some form of
colloidal association is a constituent of the complicated structure
of the rubber membrane.   The second break in the carbonic acid
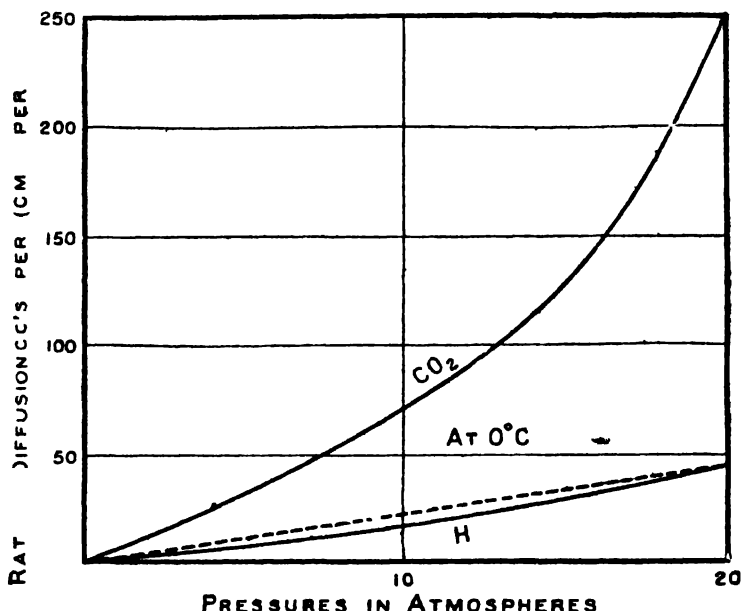
FIG. 19.

curve at – 37° C. suggests a possible combination of the membrane
with carbonic acid below this temperature.

These results were obtained with gases at the atmospheri· pressure
passing into the vacuous space of known volume behind the mem-
brane.   Working at higher pressures—up to twenty atmospheres—
this curious break in the logarithmic graph is much less evident.
The conditions of experimenting were not quite comparable, as the
gases passing through the membrane were collected at atmospheric
pressure and measured either over brine or heavy mineral oil in the
case of carbonic acid, or over water when hydrogen was employed.

When a gas-bottle charged to 10 atmospheres with carbonic acid was connected to the membrane box, Fig. 16 (*b*), the gas issued from the exit tube of the gas-box at the rate of two or three bubbles per minute.

The variation with increasing pressure at constant temperature is seen in Fig. 19.

It is definitely not quite linear in the case of hydrogen ; and with carbonic acid the rate increases at a very much greater proportion than the pressure. Comparable experiments made at fractions of an atmosphere reveal the same behaviour, though to a less degree. Wroblewski's conclusion would, therefore, seem not to be strictly true.

COMPOSITION OF PRODUCTS OF AIR DIFFUSION THROUGH RUBBER.

Since the different components of the atmosphere diffuse at different rates through rubber, it is of interest to examine the products obtained after an extended period of diffusion. The values found for the increase of oxygen percentage may be tabulated as follows :—

Time of Diffusion	Area of Membrane	Rate for Air at 15° C.		Volume of Product	Oxygen Percentage
1 day	50 sq. cm.	1·44 c.c. per sq. cm. per day		70 c.c.	46·5
4 days	50 ,,	1·44 ,,	,,	290 ,,	36
4 ,,	25 ,,	0·82 ,,	,,	82 ,,	31
5 ,,	25 ,,	1·08 ,,	,,	135 ,,	37

The presence of helium, as well as neon and hydrogen, could be readily detected in the gas passing through the membrane. For this purpose charcoal cooled in liquid air was used to maintain a low pressure behind the membrane by condensing the diffusing oxygen and nitrogen. On the side of the charcoal further from the membrane a sparking-tube of small volume was sealed, to afford the means of detecting any helium or neon and hydrogen : they would scarcely be diminished in amount by absorption in the small amount of charcoal used. The more readily to accumulate a sufficient pressure of these gases to give a good discharge, the free space in the apparatus was kept as low as possible. It was found necessary to dry the air coming into contact with the membrane, as otherwise the narrow space in the charcoal tube in liquid air became plugged with condensed ice from the water vapour diffused in from the air.

The form of apparatus found most convenient is here figured.

A is the charcoal tube about 7–8 mm. diameter and about 25 cm. long, for convenience of standing in a deep vacuum vessel in order
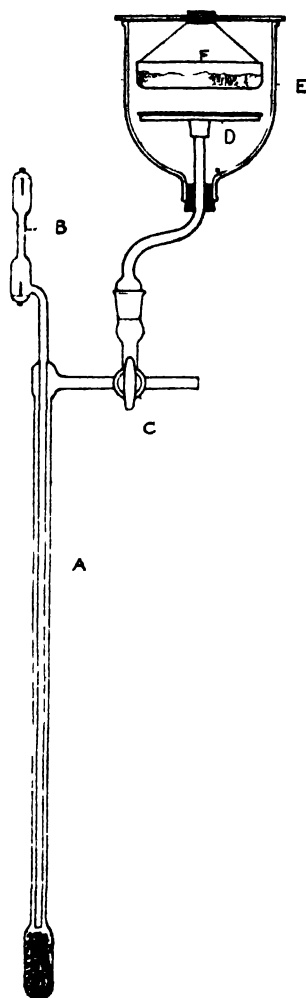
FIG. 20.

to remain undisturbed in liquid air for extended periods. A is enlarged to a bulb below sufficient to contain a gram or two of good

charcoal. Inside A is a smaller tube about 5 mm. in diameter reaching to the charcoal ; it is sealed to the top of the outer tube and continues up to the sparking-tube B. The Regnault three-way stopcock C is sealed near the top of the annular space of A by a short connection of about 2 mm. bore. The vertical branch of C terminates in a ground cone as close to the stopcock as possible. The brass cone of an indiarubber membrane support D fits this vacuum tight. To limit the free space below the membrane the drum support is reduced to very little more than the depth of a few thicknesses of stiff dried porous paper, which are placed inside to support the membrane. The remaining branch of C serves for connecting the preliminary exhaust. The membrane support passes through a cork into an inverted bell jar E, from the loose cover of which a dish F of phosphorus pentoxide is hung. The air gaining access to the membrane through the loose cover is thus dried. To equally serve this purpose the membrane may be enclosed in its gas-box, Fig. 1 (a), with the inlet tube bent down into a U immersed in the liquid air round A.

It is only necessary, after heating and exhausting out the charcoal and sparking the Pt electrodes of B, to turn C to connect D to the charcoal tube, and then arrange a flask of liquid air to keep the charcoal continuously cooled. The annular construction of A, when in the liquid air, keeps B free from any volatile impurity coming from the membrane or the stopcock lubricant.

The air diffusion rate of the membrane used was previously determined in each case ; thereby a knowledge of the amount of air diffusing through and condensed in the charcoal in any time is determined, the area of the membrane being also known.

For a fairly rapid indication, a membrane of 50 sq. cm. area, having an air rate at 15° C. of 1·44 c.c. per day per sq. cm., was employed with half a gram of charcoal. Within 12 hours the whole helium and neon spectrum was visible when a discharge was passed between the platinum wire poles of B. 36 c.c. of air would now be condensed in the charcoal. The F line of hydrogen was faintly seen, with the beginning of some nitrogen lines. This experiment continued for four days, when on removing the charcoal from the liquid air 290 c.c. of gas was obtained containing 36 per cent of oxygen.

To study the manner of growth of the gas discharge more steadily, another experiment was made with a thicker membrane of half the area, i.e. 25 sq. cm. ; the air diffusion rate was only 0·82 c.c. per day per sq. cm. A contained 2 grams of charcoal. The resulting observations were as follows :—

> 18 hours : 15½ c.c. condensed : He yellow line alone, quite bright, with much phosphorescence, therefore low pressure. Nothing further showing until

42 hours : 37 c.c. diffused in ; bright gas discharge. Helium : yellow brilliant, green feeble. Neon : orange set quite distinct. Hydrogen : very feeble F line only.

72 hours : 63 c.c. condensed. Same appearance as shown at 42 hours intensified, with F line of hydrogen quite plain.

90 hours : 78 c.c. condensed. Helium, neon, hydrogen and nitrogen all visible. Neon orange and yellow about equally intense with the complete set of 5 helium lines ; F line subdued comparatively, so also blue, green and violet nitrogen. Full red gas glow discharge with still some phosphorescence.

The day after this the neon greatly intensified, while the helium faded out in the blue and green. The hydrogen then disappeared ; then the nitrogen intensified, and the remaining lines greatly diminished.

When, instead of platinum wire poles, B has external electrodes, conveniently formed by small deposits of silver top and bottom, then the green line of helium is the first to show, and all the helium spectrum develops before anything else.

The sequence of the experiment was as follows :—

Large double film of 98 sq. cm membrane surface. Rate of diffusion for air at 15° C., 1·15 c.c. per sq. cm. per day, or 4·7 c c. per hour through the whole surface. Weight of charcoal 1½ grams.

4 hours : 19 cc. diffused in ; faint shadow of the green helium line, with much phosphorescent discharge.

9 hours .	42 c.c. in.		Helium green line well seen ; no other.
11	,,	52 ,,	Same as in 9 hours, but more definite.
22½	,,	106 ,,	All the five principal helium lines only.
23½	,,	111 ,,	Neon orange set visible in addition to the helium lines previously showing. No sign of hydrogen.

The total gas extracted from the charcoal had 40 per cent of oxygen in this case.

RELATIVE RATES OF HELIUM AND NEON DIFFUSION.

The three gases helium, neon and hydrogen are not of course affected to the same extent by charcoal at liquid air temperature. Helium is hardly absorbed at all ; neon is only very slightly taken up, whereas the condensation of hydrogen is quite appreciable. Therefore, in an equal mixture of the three gases over cooled charcoal, the helium and most of the neon would be free, while the pressure of the hydrogen would be sensibly reduced. Now, the relative proportions of the three gases present in air may be taken as 20 of neon, 5 of helium, and from ½ to 2½ of hydrogen (London air), expressed as parts per million volumes of air. If, therefore, they diffused through the indiarubber at the same rate, the neon should be apparent in one quarter the time of the helium, while the hydrogen would only appear in about twenty times the period necessary for the neon.

The second experiment just detailed showed that when the helium was visible spectroscopically in 18 hours, not until 42 hours could

the neon be seen distinctly, and then the hydrogen is also just visible. One may infer that the ratios of helium and neon diffusion are as 9 to 1, and that hydrogen and helium are nearly alike. But considering the partial condensability of the hydrogen in the charcoal, the actual hydrogen rate would be greater, as indeed is shown by the direct measurements. In the same way, having regard to the slight condensability of the neon, the above estimate of one-ninth the helium rate would be a minimum. The spectroscopic method cannot, however, be regarded as strictly reliable under such circumstances, as the electric discharge does not necessarily induce the emission of spectral lines proportionally to the several constituents.

It must also be noted that when the discharge-tube had outside electrodes, the first helium line to be seen was the green ; and that it showed in at least one-fifth of the time necessary to bring out the neon lines in these conditions, compared to about two-fifths of the period required by the tube provided with platinum wire poles, which gives the yellow helium line first and not the green. The method, nevertheless, is capable of useful extension.

PROPORTION OF " UNCONDENSABLE " GASES IN THE PRODUCT OF AIR DIFFUSION THROUGH RUBBER.

One experiment was made with the object of ascertaining the proportion of the uncondensable gases —helium, neon and hydrogen —in the total material diffusing through a rubber membrane in air. The method of condensation at $20°$ Abs. was employed as described in the Discourse a year ago.

From this it appeared that after two hours' diffusion through a membrane of 48 sq. cm. surface, with an air rate at $15°$ C. of $0·74$ c.c. per minute, the amount of uncondensable present was $17·8$ parts per million ; but that this value was increased to 120 after 4 hours, or nearly 7 times as much. The value for atmospheric air being about 27 parts per million, there would thus appear to be a five-fold increase of the uncondensable material in this diffused gas.

The total pressure of diffused gas passing into the highly exhausted McLeod gauge of 560 c.c. volume was $9·11$ mm. ; so that the partial pressure left at $20°$ Abs. was $0·0011$ mm. However, no precaution was taken to dry the air coming into contact with the membrane, as described in the previous experiments. It is therefore possible that the metal of the membrane support was attacked to some extent by the water vapour, thereby giving an increased proportion of hydrogen, so that the present result requires confirmation.

DIFFUSION THROUGH RUBBER MEMBRANES IN LIQUIDS. WATER VAPOUR TRANSMISSION.

The diffusion of water vapour has already been alluded to in connection with the necessity of drying the air over the membranes

when studying the composition of the gases diffusing for an extended period. The first rough measures on the oil manometer of the rate of water-vapour transmission, by comparing wet and dry air, seemed to indicate that at ordinary temperatures water vapour had at least forty times the rate of dry air reckoned at the same pressure, but that at high temperatures the proportion was much less. More exact determinations were necessary to settle this, and the method adopted was to weigh the diffusing water vapour after condensation in a cooled U-tube in the exhausted space behind the membrane, the cooling agent employed being liquid air or solid carbonic acid.

A preliminary trial on these lines showed that when air from the room was diffusing through a 25 sq. cm. membrane and the cooled U-tube, into the exhausted McLeod gauge, then a visible ice deposit was obtained in the U-tube in less than 10 minutes, and that nearly 30 mgms. of water were obtained in a day.

A mounted membrane of 12½ sq. cm. area was then immersed in water at 15° C. In 18 hours 36·8 mgms. of water were obtained, which is a rate of 3·93 mgms. per day through each square centimetre. To compare with the values given above for air this may be transferred into volume of water vapour reckoned at N.T.P., when the rate becomes 4·88 c.c. per day per sq. cm.

Neglecting any effect of the water immersion on the character of the membrane, and assuming that the diffusing water vapour was merely that due to the tension of water at 15° C., then we have only 12 mm. pressure instead of 760 mm. for the air diffusion. Therefore the proportional value for water vapour at an equal pressure would be 94 times that given by air, reckoned weight for weight, or 163 times in relative volumes, the figures then becoming 249 mgms., or 310 c.c. of N.T.P. water vapour.

The effect of dissolving a salt in the water round the membrane was next tried. Taking a 40 per cent solution of calcium chloride at 15° C. as an example, the rate of transmission of water vapour was reduced to 2·45 mgms. per sq. cm. per day, equal to 3·04 c.c. of N.T.P. vapour, being about 70 per cent of the rate of pure water. It may be added that the tension of water vapour from such a solution at 15° C. was found to be one-half that of water.

In contrast to the salt a colloidal substance was tried, as having no effect on the vapour pressure. Gum acacia was used as an example of this; a distinctly viscous solution of 1·07 S.G. gave the same rate very nearly as pure water on the same membrane. The actual rates per sq. cm. per day were 4·89 mgms. for pure water and 4·76 mgms. for the gum, or not more than 2½ per cent reduction.

A determination with the membrane in pure alcohol gave 56 mgms. condensed from 4½ hours' diffusion, which is a rate of 24 mgms. per sq. cm. per day, equivalent to 11·6 c.c. of alcohol vapour reckoned at N.T.P.; this is about the same rate as hydrogen

diffusing at atmospheric pressure. The tension of the alcohol being about 32 mm., the proportional rate at 760 mm. would be 570 mgms., or 275 c.c. of N.T.P. vapour, per sq. cm. per day. This is some 145 times the volume rate found for air at 15° C. on the same membrane.

TRANSMISSION THROUGH RUBBER OF GASES DISSOLVED IN THE IMMERSING LIQUIDS.

The rate of diffusion through the indiarubber of gases dissolved in various liquids was investigated along with the above measurements of liquid vapour transmission. Various gases were dissolved in the water, alcohol, etc., in which the membrane was immersed. The increase of gas pressure was measured in the exhausted McLeod gauge to which the membrane and condensing U-tube were connected, and thereby the amount of diffusion of the dissolved gases through the membrane is revealed. Instead of a gas rate of the order of 2 c.c. per day per sq. cm. obtained with the membrane exposed in air, the following values were obtained :—

I.—WATER AND AQUEOUS SOLUTIONS ROUND MEMBRANE.

	c.c. per day per sq. cm.
Freshly boiled out, distilled water	0·09 to 0·04
Air saturated distilled water	0·414
Hydrogen saturated distilled water	1·62
Carbonic acid saturated distilled water	15·5
Cane sugar solution, 30 per cent. Freshly boiled ...	0·017
„ „ 36 „ „	0·011 to 0·006
„ „ 36 „ Exposed to air 2 days	0·09
Gum acacia solution, S.G. 1·07. Freshly boiled ...	0·010
Calcium chloride, 60 per cent solution. Freshly boiled	0·007
Hydrochloric acid solution, ⎰ Not boiled ; ⎱ 0·19, falling	
3 per cent ⎱ metal protected ⎰ to 0·06	
Acetic acid solution, 3 „ ⎰ by rubber ⎱ ...	0·90
Formic „ 3 „	0·45

II.—ALCOHOL.

Freshly boiled under exhaust	0·4 to 0·6
Air saturated	1·26
Hydrogen saturated	3·5
Carbonic acid saturated	25·0
1 per cent alcohol in water, boiled	0·05
5 „ „ „ „	0·11
10 „ „ „ „	0·27

III.— GLYCERIN.

Immersed in 96 per cent glycerin	0·0084
„ 50 „ „ (freshly boiled water used)	0·027
„ 50 „ „ air saturated	0·09

It would thus appear that the relative rates of gases in solution is not so low as their proportional lowering of volume concentration

in the liquid, for water at 15° C. dissolves about one-sixtieth of its volume of air or hydrogen, but the rate of diffusion from air-saturated water is only reduced to one-quarter of the rate in air. Roughly the same relation is shown by hydrogen. The effect of expelling the gases by boiling is very marked, especially in the case of solutions. The effect of glycerin in checking diffusion is also very evident.

The behaviour of alcohol is quite the opposite. Air goes through the membrane equally rapidly whether alcohol is round it or not. By freeing the alcohol from dissolved gases, the diffusion is checked, as is the case with water; but in about one hour has regained its initial rate.

[J. D.]

Friday, March 26, 1915.

THE RIGHT HON. LORD RAYLEIGH, O.M P.C. D.C.L. LL.D. D.Sc. F.R.S., Professor of Natural Philosophy R.I., in the Chair.

PROFESSOR SIR J. J. THOMSON, O.M. LL.D. D.Sc. Pres. R.S. *M.R.I.*, Professor of Natural Philosophy, R.I.

Experiments on Slow Cathode Rays.

ELECTRIC waves and Röntgen rays are two of the most important discoveries in Modern Physics. Though the two radiations differ so widely both in their properties and methods of production, there is very strong evidence in favour of the view that both are vibrations of the same nature as visible light, and that though the wave length of electrical waves might be long enough to reach across London, while that of Röntgen rays is of the order of the radius of an atom, they were all members of the same family. The question arises whether the very wide gap between these extreme cases is filled up continuously with waves of different kinds, or where there are gaps in this long interval. Electric waves have been produced whose wave length is only a few millimetres, and this limit could no doubt be lowered if special experiments were made with that object; on the other hand, Rubens has isolated waves in the infra-red spectrum which have a wave length as long as one-third of a millimetre. There is thus no gap between electric waves and light waves. Is this true for the other end of the light spectrum, i.e. is there continuity between light waves and Röntgen rays? The shortest wave lengths known for light waves are those discovered by Lyman in what is known as the Schumann region of ultra-violet light. They have a wave length of about one ten-thousandth of a millimetre, while the longest wave length yet measured for Röntgen rays is of the order of one-millionth of a millimetre; there is thus a gap of about seven octaves between the two. This gap up to the present has not been systematically investigated, but its study promises to be of especial interest. The rays in the Schumann region and very soft Röntgen rays

show considerable approach to each other in their properties.   Both
kinds of rays ionise gases when they pass through them, while light
in the visible region of the spectrum does not do so.   Unfortunately,
too, for the experimenter, both are so readily absorbed that they are
unable to penetrate even very thin layers of air, so that it is a matter
of very considerable difficulty to investigate their properties.   Both
kinds of rays produced strong chemical and physiological effects when
their energy is absorbed in the medium through which they are
passing.   Thus both, as I can easily show by holding starch paper in
their neighbourhood, produce ozone ; both, too, are disastrous to some
of the lower organisms.   Indeed, some of the latter under their
influence undergo the most disconcerting experience an aquatic
creature can suffer, for they gradually, when exposed to these rays,
dissolve away in the water in which they are living.   The study of
the rays in this gap may thus become of high biological and medical
importance.

The method I have used to produce rays between Schumann rays
and ordinary Röntgen rays is to bombard a metal target with very
slow cathode rays.   The cathode rays which produce the Röntgen rays
in an ordinary Röntgen ray bulb have speeds corresponding to 20,000
volts or so and upwards ; the cathode rays I have used have speeds
corresponding to from 5 to 2000 volts.   It is well known that the
greater the speed of the cathode particle the harder the Röntgen rays
they produce.   I can show this very distinctly by using a special and
very convenient form of Röntgen ray bulb—the Coolidge tube—for
the loan of which I am indebted to Messrs. Cossar.   The essential
feature of this tube is that the cathode produces its own supply of
cathode particle, as it consists of a tungsten filament heated to
redness by an independent heating circuit.   The white hot tungsten
gives out cathode rays which have no velocity when they start from
the cathode ; the velocity is communicated by the potential difference
between the cathode and anode.   As this is increased the velocity
acquired by the particles before they strike against the target is also
increased.   The number of cathode particles does not depend upon
this potential difference, but is determined solely by the temperature
of the tungsten spiral.   The vacuum in the bulb is an exceedingly
good one, so good that you do not see the ordinary green phosphor-
escence on the glass when the bulb is in action.   If I hold my hand
in front of a platino-cyanide screen, and gradually increase the speed
of the cathode particles by increasing the potential difference, you
will see that at low speeds very few Röntgen rays reach the screen
through my hand ; as I increase the speed some get through the
flesh, but are stopped by the bones, and at the very highest speeds an
appreciable amount gets through the bones themselves.

I will now pass on to consider the production of soft Röntgen
rays by the impact of slow cathode rays.   The first method was as
follows :—Fig. 1 is a Wehnelt cathode ; the anode A is a brass rod

with a hole bored through it to allow the cathode rays to pass through and strike against the target B ; this is a copper plate which is at the end of and in metallic communication with a cylinder of wire gauze. The variation in the speed of the cathode particles is produced by putting between this gauze and the anode a potential difference tending to stop the rays. Thus, if V_1 is the P.D. between the anode and cathode, V_2 that between the anode and the gauze, the energy of the cathode rays when they strike the target is proportional to V_1-V_2. To detect any radiation coming from the target a camera was placed at the end of the side tube T ; a slit was put in front of the photographic plate, and half of it covered by thin slices
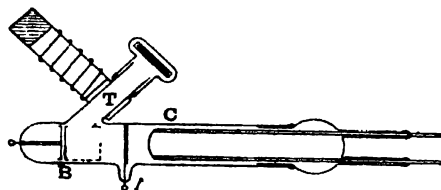
FIG. 1.

of paraffin wax, collodion, mica, glass, or fluorite, so as to be able to estimate the penetrating power of the radiation. A magnet was placed between the target and photographic plate, so as to deflect from the latter any corpuscular radiation from the target. The vacuum was made as low as possible by charcoal and liquid air ; it was so low that no luminosity could be detected between the anode and the target. The plates used were Schumann plates. The times of exposure, which varied from one minute to two hours, were chosen so as to make the energy in the cathode rays striking against the target during the time of exposure constant. Thus, for cathode rays which had fallen through 10 volts the time of exposure would be ten times that for those which had fallen through 200 ; the latter gave dense photographs with an exposure of two minutes. I have obtained photographs with potential differences as low as 10 volts. These are not due to ordinary light coming from the discharge tube, for (1) they are not obtained when the beam of cathode rays is deflected from the target by a magnet ; and (2) the rays which produce them are quite unable to penetrate very thin films of glass. To test whether or not they were due to corpuscular radiation from the target two methods were employed. First, a magnet was placed between the target and the photographic plate so as to deflect the corpuscular radiation from the plate ; this did not affect the photographs. The second method was to place between the target and the photographic plate a pair of parallel plates and apply to them a

potential difference of 1000 volts. The intensity of the photographs was not diminished when all the radiation which fell on the plate had passed through this strong electric field which would have stopped any charged particles. With regard to the penetrating power of this radiation, I have been able just to detect the photographic effect behind a film of collodion thin enough to show the colours of their plate, when the cathode rays had energy corresponding to 40 volts. When the energy corresponds to 80 volts the effect behind the collodion, and also behind a film of paraffin wax $\frac{1}{4}\mu$ thick, is quite appreciable, while after 200 volts there is very considerable penetration of the paraffin and collodion films.

This photographic method did not, however, lend itself easily to quantitative measurements. For this purpose I made use of the ionisation of gases produced by these soft Röntgen rays. The rays instead of falling on a photographic plate passed through a thin window into a tube leading into a chamber containing SO_2 or some other gas giving a large number of ions. The quantity of gas was sufficient to absorb all the rays, so that the number of ions produced is a measure of the energy which has passed into the ionisation vessel. Considerable difficulty was found in finding a suitable window, as the discharge tube itself was a very good vacuum, while it was necessary to have a finite pressure of gas in the ionisation chamber. The film had to be stout enough to stand a difference in pressure of a few millimetres of mercury on the two sides, and yet be thin enough to transmit the very easily absorbed radiation. The difficulty was solved by a device due to my assistant, Mr. E. Everett. Very thin films of celluloid were prepared by dissolving celluloid in amyl-acetate and pouring a thin layer of the solution on liquid mercury; this leaves the edges of the films free, if they are held tight the film cracks as it dries. Films prepared in this way were so thin that they showed the colours of thin plates. The other method is to measure the energy of the radiation given off from a target struck by the cathode rays. It is known that when ultra-violet light or Röntgen rays fall on a plate of metal, the plate emits negative electricity, and the quantity of this emitted is proportional to the energy as long as the type of radiation is constant. To apply this method the tube T, instead of leading to a camera, lead to a spherical bulb, silvered on the inside, and at the centre of the bulb there was an insulated plate of metal connected with a Dolezalik electrometer; the silvered bulb was maintained at a positive potential of several hundred volts positive to earth, while the plate of metal at the centre was, before the radiation fell upon it, at the same potential radiation as the earth. When the radiation fell upon it, it lost negative electricity, the amount of which could be determined from the deflection of the Dolezalik electrometer. In order to stop any charged particles passing from the discharge tube into the silvered vessel, parallel plates of metal were placed in the tube T, and a potential difference of 600 volts was maintained between them.

With each of these methods the following results were obtained. The energy in the radiation from the target is very small until the cathode rays have an energy corresponding to about 15 volts. The energy then rises quickly with the potential ; then, when the energy is measured by the second method, reaches a maximum, and then decreases very slowly. This refers to the energy in the Röntgen radiation emitted by the target. It is known, however, that when a target is struck by cathode rays, negative electrons moving at a much slower speed than the primary cathode rays are also given out, and the variation in the number of these negative electrons with the voltage of the incident cathode rays has been investigated by Leitz, Campbell and others. This variation is very similar indeed to the variation in the intensity of the Röntgen radiation, for it begins between 10 and 15 volts, reaches a maximum between 200 and 300 volts, and then slowly decreases. The number of electrons does not depend on the nature of the target (carbon targets are an exception). As far as our experiments go at present a similar statement is true for the Röntgen radiation produced by the cathode rays ; this does not change much when one metal replaces another for the target.

The close correspondence between the emission of negative electrons and of the soft Röntgen radiation supports a view of the origin of this radiation which I expressed some years ago ; it is that the radiation originates in the return of an electron to an atom or a molecule which has been ionized, the kind of vibration depending on the nature of the electron which has been ejected when the atom was ionized. If this was one of the electrons on the surface, the radiation would be in the region of ordinary light : if it was from the innermost ring of electrons in the atom it would correspond to the K radiation ; if from a ring not so close to the centre the L radiation ; and so on. As each unit of radiation emitted corresponds to the return of a free electron, it is evident that there would be a close connection between the number of free electrons produced by the cathode rays and the energy in the Röntgen radiation due to those rays ; as we have just seen such a correspondence does exist. We may hope to gain important information about the atom from the study of these soft radiations, for they are given out by the electrons not far from the surface of the atom, and it is just these electrons which determine the chemical properties of the atom.

[J. J. T.]

Electrons and Heat.

When electrified bodies are heated they are found to lose the power
of retaining an electric charge. The charge leaks away from their
surfaces. This is not a novel phenomenon. It has been known for
nearly two centuries that solids glowing in air are capable of dis-
charging an electroscope. Thus you observe that the electroscope is
at once discharged when I bring near it a red-hot poker withdrawn
from the furnace on the lecture-table. These effects are due to the
emission of ions by the hot solids. For example, if the electroscope
is negatively charged, it draws positive ions from the hot poker, and
so becomes discharged.

Most bodies when heated in air at low temperatures emit only
positive ions. At sufficiently high temperatures ions of both signs
are emitted simultaneously. We can show this by a simple experi-
ment in which the hot body consists of a loop of platinum wire and
acts as its own electroscope. When a charged rod is brought near
the loop a charge of opposite sign is induced on the latter, which is
thus deflected owing to the electrostatic attraction of the rod. When
the loop is cold this happens whatever the sign of the charge on the
rod. If the wire is at a dull red heat it can only be deflected by a
positively charged rod. When a negatively charged rod is brought
near it the emission of positive ions causes the induced positive
charge at once to stream away. Thus the wire is incapable of retain-
ing a positive charge, and so no deflection is produced by a negatively
charged rod. At very high temperatures you observe that the loop
is undeflected whatever the sign of the charge on the rod. The wire
is now liberating both positive and negative ions, and so is unable to
retain either a positive or a negative charge.

If these effects are investigated in a vacuum, instead of in air at
atmospheric pressure, it is found that the emission of positive ions
gradually disappears with continued heating, so that a wire which
has been well glowed out in a vacuum emits only negative ions in
appreciable quantity. Thus, if we repeat the last experiment with

an incandescent lamp, using one in which the filaments are not anchored, we see that the loops are attracted by a negatively charged rod, but not by one which is charged positively. They show, in fact, a behaviour which is precisely opposite to that of a wire at a dull red heat in air.

Now let us consider the nature of the ions which carry these thermionic currents, to use a term which I have ventured to apply to the currents which leak away from the surfaces of hot bodies in this manner. As is well known, the negative electrons which play such an important part in physical phenomena are very readily deflected by moderate magnetic fields, whereas ions of atomic or greater magnitude are not. I have here an arrangement which will enable us to apply this test to the ions emitted by hot bodies. An exhausted tube carrying a horizontal hot wire is placed in a vertical electric field. The electric field is arranged so as to drag the negative ions emitted by the wire to a suitable electrode, whence they flow through a galvanometer whose deflection is registered by the spot on the screen. Around the tube an electro-magnet is arranged, so that, when it is excited, there is a horizontal magnetic field which tends to curl up the paths of the ions. If I now switch on the electro-magnet, you observe that the current is at once reduced to a small value, showing that the magnetic field curls up the paths of the ions, so that they are now unable to reach the electrode. The carriers of this negative discharge are, in fact, electrons.

I have here a second tube, arranged to give a conveniently large positive discharge   When this is tested by the electro-magnet in a similar way, the magnetic field is found to have no influence on the thermionic current. The positive ions are, in fact, much more massive than the electrons ; more elaborate experiments have shown that they are charged atoms.

We see from these experiments that the negative emission is characterized by the electronic nature of the carriers and by its permanence in a vacuum. The presence of a gaseous atmosphere is not necessary in order to maintain these currents. Thus the electrons must come from the heated body itself. I believe that this emission is a process which is closely analogous to evaporation. The essence of evaporation, of a liquid for example, lies in this : that, as the temperature is raised, the molecules acquire sufficient energy to overcome the forces which attract them to the liquid, and so become free molecules of the vapour. We know that all material substances contain electrons, and it is not unreasonable to expect them to behave, when the temperature is high enough, in a way analogous to the molecules of a liquid. Another analogy, in some ways more accurate, would liken the emission of electrons to the reversible evolution of a gas by the decomposition of a solid such as calcium carbonate. The similarity of this process to evaporation is well known to chemists.

This position is strengthened when we examine the way in which the electron emission depends on the temperature of the hot body. This may readily be done by surrounding the hot wire with a cylindrical electrode to catch the electrons, which then flow through a galvanometer whose deflection measures their number. The hot wire is arranged to lie in one arm of a Wheatstone's bridge ; so that its temperature may be deduced from its resistance. Innumerable experiments with different substances have shown that this emission increases with great rapidity as the temperature rises, just as does the corresponding phenomenon in the case of evaporation. The correspondance is, in fact, exceedingly close. We may take the rate of emission of molecules from the surface of an evaporating liquid to be proportional to the vapour pressure. The proportionality is not exact, but it is sufficiently so for our purpose. The crosses on the next slide represent values of the vapour pressure of water, on the vertical scale, plotted against the corresponding temperatures from 0° C. to 90° C, on the horizontal scale ; whilst the circles represent the emission currents from platinum plotted similarly against temperature over the range 1000° C to 1250° C. All the points lie on the same continuous curve within the limits of experimental error. To bring about this coincidence, it is, of course, necessary to plot the temperatures on quite different scales in the two cases, but the agreement demonstrates in a simple way the similarity of the laws which govern the temperature variation in both cases.

Numerous cases of electron emission have now been examined, and it has invariably been found, provided there is no reason to suspect changes in the chemical nature of the emitting surface, that the relation between the current i and the absolute temperature T is expressed by a very simple equation. This is

$$i = A \, T^{\frac{1}{2}} \; exp - \frac{b}{T}$$

or

$$\log i - \tfrac{1}{2} \log T = \log A - \frac{b}{T},$$

where A and b are constant quantities for any particular substance. The theory underlying this equation shows that the quantity b is very nearly equal to half the energy change, expressed in calories, when one gram molecular weight of the electrons is emitted. Pursuing the analogy with evaporation, this quantity may be called the molecular latent heat of evaporation of the electrons. It is not, however, with the theory underlying this equation that I particularly wish to concern you now ; but I do wish to impress the fact that this formula is not an empirical affair covering a small range of temperature and current. The most recent measurements,* made with tungsten, have

* *cf.* K. K. Smith, Phil. Mag. vol. 29, p. 102 (1915)

shown that the formula expresses the results within the limits of experimental error, over the range of temperature from 1050° K. to 2300° K. At the lowest temperatures the currents were less than one-millionth of a microampere per square centimetre, and had to be measured with a sensitive electrometer, whilst at the highest temperatures they were comparable with one ampere per square centimetre, and could be measured on a commercial ammeter. Thus the equation holds true whilst one of the variables changes by the enormous factor of 10^{12}. There are not many physical laws which will stand so severe a test as this.

Let us now turn to some other consequences of the hypothesis that the emission of electrons is analogous to evaporation. One of the familiar effects of evaporation is to cool the liquid which gives off the vapour, owing to the latent heat of vaporization. In an exactly analogous manner, a wire which is giving off electrons will be cooled thereby. I think I can succeed in demonstrating this effect to you, although the lowering of temperature to be looked for is not very large, and delicate means have to be employed to detect it. This tube contains a hot tungsten wire, which is made to act as its own thermometer by placing it in one arm of a sensitive Wheat-stone's bridge. Minute changes in its resistance can thus be measured. The bridge is balanced with the electrode surrounding the hot wire negatively charged ; so that the thermionic current does not flow. If I reverse the potential and thus start the thermionic current, keeping the heating current constant, you observe a sudden deflection of the spot of the bridge galvanometer. The direction of this deflection corresponds to a reduction of the resistance of the hot wire, and thus to a lowering of its temperature. By experiments of this kind, Professor Cooke and I succeeded in measuring the latent heat of evaporation of the electrons directly

Just as a liquid is cooled by evaporation, so it is heated to a corresponding extent when the vapour condenses. In fact, an elementary experiment with which every student of physics is familiar, consists in measuring the latent heat of evaporation by blowing steam into water. A precisely analogous experiment can be made with electrons. A large electron current from a hot wire is driven on to a fine strip of the metal, whose latent heat of condensation for electrons is to be tested. The cold strip is made to act as its own thermometer by placing it in one arm of a sensitive Wheatstone's bridge. When the hot wire is charged positively there is no electron current to the strip, and the bridge is balanced under these conditions. The wire is then charged negatively, so as to make the electrons flow on to the strip. There is then an increase in resistance, due to the heat liberated by the condensation of the electrons, which is measured. In these experiments only part of the observed change of resistance arises from the effect under consideration. The remainder is caused by the kinetic energy given to the electrons by

the auxiliary field used to drive them from the hot wire to the strip. This, however, is easily determined and allowed for.

I have now indicated to you three independent methods of deducing the values of the latent heat of emission of the electrons. Let us see how the latest and most accurate values obtained by these methods agree with one another. The numbers found, and the names of the experimenters responsible for them, are shown in the following table :—

Values of Latent Heat of Emission reduced to Equivalent Temperatures.

1. From the temperature variation of the rate of emission.
    Tungsten (Langmuir) $10 \cdot 5 \times 10^4$ - $11 \cdot 1 \times 10^4$ calories per Mol.
    Tungsten (K. K. Smith) $10 \cdot 94 \times 10^4$ calories per Mol.
    Platinum (various) 12×10^4 – 16×10^4 calories per Mol.

2. From cooling due to emission.
    Tungsten (Cooke and Richardson) $11 \cdot 24 \times 10^4$ calories per Mol.
    Tungsten (Lester) $11 \cdot 04 \times 10^4$ calories per Mol.
    Platinum (Wehnelt and Liebreich) $13 \cdot 9 \times 10^4$ – $14 \cdot 5 \times 10$ calories per Mol.

3. From heating due to condensation.
    Platinum (Richardson and Cooke) $13 \cdot 5 \times 10^4$ calories per Mol.

Unfortunately, the vacuum value for platinum given by the first method is still uncertain, owing to complications caused by gaseous contaminants. Except for this, the agreement between the different methods leaves nothing to be desired.

We come now to the very interesting question of the velocity and kinetic energy which these electrons possess when they are emitted. The fact that they are electrically charged enables us to find out a great deal more about their emission velocities than we can do in the corresponding case of the emission of ordinary molecules. By applying an external electric field we can influence the motion of the emitted electrons, and the precise nature of the effect exerted by the field depends on the velocity with which the electrons are shot off from the hot body. It is clear that we have no such method of controlling the motion of ordinary molecules.

I shall now consider one of the arrangements which has been used in applying these principles to the analysis of the emission velocities. The hot emitting surface is a small strip of platinum, electrically heated, which lies at the centre of a much larger metal plate. The upper surfaces of the strip and the plate are flush with

each other, and are maintained at the same potential. Vertically above this lower plate and a short distance away from it is a parallel metal plate connected to the insulated quadrants of an electrometer. An arrangement is provided by which a suitable difference of potential can be maintained between the two plates, so as to *oppose* the motion of the electrons from the strip towards the upper plate. It is clear that if the electrons have no velocity when they are emitted, any retarding field, however small, will be sufficient to stop them from reaching the upper plate and charging up the electrometer. If, on the other hand, they are shot off with a definite component of velocity normal to the strip, they will reach the upper plate, provided the corresponding kinetic energy exceeds the work they have to do to overcome the opposing difference of potential. Thus, if the electrons are not at rest when they are emitted, they will give rise to currents capable of flowing *against* an applied electromotive force if this is not too large. I have here an arrangement, similar in principle to that just described, which will enable me to show to you the existence of these currents flowing against an applied electromotive force. The platinum strip is replaced by a very short tungsten filament, the upper plate by a surrounding cylinder, and the electrometer by a galvanometer. The apparatus is thus different in detail from that already referred to, but the principle is the same. You observe that the current is largest when the opposing difference of potential is zero, and falls off uniformly and rapidly as the potential difference is increased. By increasing the temperature 1 can cause a considerable current to flow against an opposing difference of potential of one volt.

The experiments just referred to are a kind of electrical analogue of the high jump, in which the measuring tape is replaced by a voltmeter. Corresponding to each emission velocity there is a definite equivalent voltage. The fact that the current falls off continuously as the opposing voltage increases shows that the electrons are not emitted with a single velocity, but with different velocities extending over wide limits. Careful experiments of this kind have enabled us to discover what proportion of them are shot off with velocities within any stated limits, to determine, in fact, what is the Law of Distribution of Velocity among the emitted electrons.

More than fifty years ago Maxwell concluded, from rather abstruse theoretical considerations, that the velocities of the molecules of a gas or vapour should not all be equal, but should be distributed in a certain way about the average value. This law, known as Maxwell's law of distribution of velocity, is somewhat similar to that which governs the density of bullet-marks on a target at different distances from the bull's-eye. The theoretical considerations which led Maxwell to establish this law for gases apply equally to the atmospheres of electrons outside hot bodies. Let us see whether the results of our experiments agree with Maxwell's predictions or not. If the law of

distribution of the normal velocity component for the emitted elec-
trons is that given by Maxwell, it is necessary (and sufficient) that
the currents i_1 and i_2, which flow against potentials V_1 and V_2
respectively, should satisfy the equation

$$\log \frac{i_1}{i_2} = \frac{Q}{RT} (V_1 - V_2),$$

where R is the constant in the equation $pv = RT$ of a perfect gas,
and Q is the quantity of electricity which liberates half a cubic centi-
meter of hydrogen at 0° C. and 760 mms. in a water voltameter.
The requirements of this formula are found to be fully satisfied by
the results of the experiments.   Thus the logarithms of the ratios of
the currents are found to be accurately proportional to the differences
in the corresponding opposing potentials at a given temperature.
Again, since Q is a well-known physical constant and the value of T
was estimated during the experiments, we can use the experimental
data to obtain a value of the gas constant R.   Eight experiments,
made under conditions as varied as possible, when treated in this
way gave values of R which varied between the extreme limits
$3 \cdot 08 \times 10^3$ and $4 \cdot 46 \times 10^3$ ergs per c.c. per deg. C.   These values
exhibit a rather wide variation which, however, is believed to be
fortuitous, so that the mean value should be much more accurate.
The mean of the eight values gives $R = 3 \cdot 72 \times 10^3$, whereas the
number given by the gas equation is $R = 3 \cdot 711 \times 10^3$ in the same
units.
     The fact that the value of the gas constant can be deduced in
this way from purely electrical measurements must be regarded as a
remarkable confirmation of the general position.   The results of
these experiments, and others of a similar nature which I have not
time to describe, show not only that the velocities of the electrons
are distributed about the average value in accordance with Maxwell's
law, but also that the emitted electrons are kinetically identical with
the molecules of a hypothetical gas of equal molecular weight at the
temperature of the hot metal.   The experiments referred to formed,
so far as I am aware, the first direct experimental demonstration of
the truth of Maxwell's law of distribution of velocities, and, although
many of the consequences of this law have been made visible by
the beautiful experiments of Perrin on the Brownian movement, I
believe that they still furnish the most direct experimental verification
of its truth.
     Quite recently a number of experimenters have called in question
the general position which I have taken as to the nature of the
process of electron emission from hot bodies, and have asserted that
this effect is caused by chemical action between the hot solid and
traces of contaminants, usually supposed to be gaseous, which have
access to it.   Whilst I feel that the value of the evidence in favour

of the latter hypothesis has, generally speaking, been greatly over-estimated, it would take too long to discuss this question with the completeness which it demands. I shall therefore content myself with directing your attention to some experiments with tungsten filaments which prove that only an insignificant fraction, if any, of the emission from this substance can be attributed to chemical action.

Tungsten is peculiarly suited to these experiments on account of its great refractoriness. It can be heated in a vacuum for considerable periods at temperatures so high that all known impurities are volatilized out of it. The preliminary treatment of the experimental lamps furnishes some novel features which may prove of interest. The ductile tungsten filaments are electrically welded to the supporting leading wires in an atmosphere of hydrogen. After mounting, the lamps are exhausted in a vacuum furnace (with an external air pressure of about 1 cm.) at 550–600° C. for about 24 hours until the evolution of gas becomes very small. A Gaede pump is used for the internal exhaust at first, and, later on, liquid air and charcoal in addition. In the final stages the tungsten is glowed at about 3000° absolute, and, for the best results, the anode is heated by subjecting it to an intense electron bombardment from the hot wire. The conditions as to freedom from gaseous contamination which have been attained in this way are far superior to those which result from any other method of treatment.

With lamps thus prepared I have carried out simultaneous measurements of the rate of emission of electrons on the one hand, and either of the variation of the pressure of the gas present or of the rate of loss of matter by the filament on the other. Particular experiments have led to the following numbers : —

(1) For each molecule of gas given off the number of electrons emitted by the filament may be as high as 260,000,000.

(2) At each impact of a gas molecule with the filament 15,000 electrons would have to be emitted, and

(3) Each atom of tungsten which disappears from the filament would have to cause the emission of 984,000 electrons.

The magnitude of these numbers entirely precludes the possibility that chemical action plays any significant part in this emission. Again, the *mass* of the electrons lost by a filament may exceed the mass of tungsten lost in the same interval, proving that the emitted electrons are not furnished *at the expense of* the tungsten. They must, therefore, flow in from outside points of the circuit. Thus these experiments furnish a direct proof that the electric current in metals is carried by moving electrons. The mechanism of metallic conduction becomes more mysterious every day, but this, at any rate, is a fact which has to be reckoned with.

Perhaps I can drive these matters home to you more effectually by means of a simple experiment, which shows that these electron

currents from tungsten in high vacua are not minute affairs requiring elaborate apparatus for their detection, but, at high temperatures, are of such magnitude as to be worthy of the consideration of the practical electrician. I have here a tungsten lamp, containing a filament 14 mm. long and about 3 mils. in diameter, in series with an ammeter, a resistance, a battery, and a second ammeter. They are arranged in the order named, so that there is an ammeter at each end of the lamp. In addition there is a side line from the cylindrical electrode of the lamp, which can be switched through either a millammeter or an electric bell to the positive end of the battery. There is no auxiliary voltage in this side line. When I turn the current on, you observe that the ammeters read differently, showing that more current is flowing into the filament at one end than out of it at the other. The difference is, in fact, equal to the electron current which flows into the wire sideways and is registered by the millammeter. Those of you who cannot see the instruments will, at any rate, hear the electric bell when I switch the electron current through it. With a lamp which was somewhat better designed for the purpose than the present one, I have recorded a current of 0·7 ampere at one end, 0·45 at the other, and 0·25 in the branch circuit. So far as my experience goes, the only limit to the size of these electron currents is that which is set by the magnitude of the current which fuses the filament, provided the requisite driving voltage is available.

[O. W. R.]

Friday, June 4, 1915.

CHARLES HAWKSLEY, Esq , M.Inst.C.E., Vice-President,
in the Chair.

PROFESSOR SIR ERNEST RUTHERFORD, LL.D. D.Sc. F.R.S. *M.R.I.*
(Nobel Laureate).

Radiations from Exploding Atoms.

IT is now well established that the radio-active substances are under-
going spontaneous transformation, and that their characteristic
radiations—the a, β, and γ rays—accompany the actual disintegra-
tion of the atoms. The transformation of each atom results from
an atomic explosion of an exceedingly violent character, and in
general results in a liberation of energy many million times greater
than from an equal mass of matter in the most vigorous chemical
reaction.

In the majority of cases the atomic explosion is accompanied by
the expulsion of an actual atom of matter—an a particle – with a
very high speed. It is known that the a particle is an atom of
helium which carries two unit positive charges, and which leaves the
atom with a velocity of about 10,000 miles per second. In some
transformations no a particle is ejected, but its place is taken by a
swift β particle or electron. These β rays carry with them a large
amount of energy, for in some cases they are expelled very close to
the velocity of light, which is the limiting velocity possible for such
particles. The expulsion of high-speed β particles is usually accom-
panied by the appearance of γ rays, which correspond to X-rays,
only of greater penetrating power than has so far been obtained
from an X-ray tube even when a high voltage is employed. The
emission of energy in the form of γ rays is not negligible, for in
some cases it is even greater than the energy emitted in the form
of high-speed β particles, and may amount per atom to as much as
20 per cent. of the energy released in the form of a swift a particle.

By the application of a high voltage to a vacuum tube it is
quite possible to produce types of radiation analogous to those
spontaneously arising from radium. For example, if helium were
one of the residual gases in the tube, some of its atoms would
become charged, and would be set into swift motion in the strong

electric field. In order, however, to acquire a velocity equal to the velocity of expulsion of an α particle, say, from radium C, even in the most favourable case nearly four million volts would have to be applied to the tube.

In a similar way, in order to set an electron in motion with a velocity of 98 per cent. the velocity of light, at least two million volts would be necessary. As we have seen, it has not so far been found possible to produce X-rays from a vacuum tube as penetrating as the γ rays. The study of the radiations from radio-active substances is thus of especial interest, not only for the information obtained on the structure of the atoms themselves, but also in providing for investigation special types of radiation of greater individual intensity than can be obtained by ordinary experimental methods. The enormous energy of motion of swift α and β particles must exist in the atom before its disintegration, either in a potential or a kinetic form, and may arise either from the passage of the charged particles through the intense electric fields within the atom, or from the very swift motion of these particles within the atom before their release. In any case, there can be no doubt that electric fields, and possibly magnetic fields, of enormous intensity exist within the very small volume occupied by the essential structure of the atom—fields many million times greater in intensity than we can hope to produce in laboratory experiments.

In order to explain certain experimental results, I have suggested that the main mass of the atom is concentrated within a minute volume or nucleus, which has a positive charge, and is of dimensions exceedingly minute compared with the diameter of the atom. This charged nucleus is surrounded by a distribution of electrons which may extend to distances comparable with the diameter of the atom, as ordinarily understood. The general evidence indicates that the α and primary β particles are expelled from the nucleus, and not from the outer structure of the atom. If this be the case, the α particle which carries a positive charge would have its velocity increased in passing through the strong repulsive field surrounding the nucleus ; on the other hand, the β particle which carries a negative charge must be retarded in its escape from the nucleus, and must possess great initial energy of motion to escape at all. There appears to be no doubt that the penetrating γ rays have their origin in some sort of disturbance in the rings of electrons nearest to the nucleus, but do not represent, as some have supposed, the vibrations of the nucleus itself.

α RAYS.

A brief account was given of the recent work of Rutherford and Robinson in determining with accuracy the velocity of expulsion of the α particles from certain radio-active substances. This was done

by measuring the deflection of a pencil of α rays in strong magnetic and electric fields. With the aid of intense sources of radiation, it was found that the value of the E/M—the ratio of the charge carried by the α particle carried to its mass—was 4820 units, a value to be expected if helium has an atomic weight 4 and carries two unit charges. This experiment also shows that the mass of the flying positive particle is not affected appreciably by its swift motion. From known data the initial velocity of the expulsion of the α particles from all other radio-active substances can be deduced with accuracy.

If the expulsion of an α particle from an atom is the result of an internal explosion, we should anticipate, from the analogy of a shot from a gun, that the residual atom would recoil in a direction opposite to the escaping β particle. The existence of these "recoil" atoms can be shown in a variety of ways, for the velocity of recoil is sufficient to cause the atoms to leave the surface on which they are deposited and to pass through a considerable distance in air at a pressure of one millimetre before they are stopped. It is to be anticipated that the momentum of a recoiling atom should be equal and opposite to that of the escaping α particle. Since the deflection of a charged particle in motion in a magnetic field is inversely proportional to its momentum, the deflection of a stream of recoiling atoms should be the same as for the α particles if the atoms carry the same charge. Dr. Makower has examined the deflection of a pencil of recoil atoms in a magnetic field, and found it to be exactly half of that due to the α particle, proving definitely that the recoiling atom carries only one unit of positive charge in place of two for the α particle.

We thus see that the simple application of momentum enables us to deduce the mass and energy of the recoiling atoms. Since the mass of the radio-active atoms is about fifty times that of the α particle, the velocity, and also the energy, of recoil is only about one-fiftieth of that of the escaping α particle. In a similar way, it can be shown that the ejection of a swift β particle should cause a vigorous recoil of the atom, though not so marked as in the case of the more massive α particle.

β Rays.

During the last few years notable advances have been made in our knowledge of the mode of emission of β particles from radio-active atoms. The work of Baeyer, Hahn, and Meitner, and of Danysz, has shown that the β rays from a radio-active substance like radium B or radium C contain a number of definite groups of rays which are expelled with definite velocities. This is best shown photographically by examining the deflection of a pencil of β rays in a magnetic field. In a uniform field, each of the groups of rays

describes a circular path the radius of which is inversely proportional to the momentum of the β particle. By the application of special methods it has been found possible to obtain a veritable spectrum of the β rays. The spectrum of the β rays from radium B and radium C has been very carefully examined by the writer and Mr. Robinson, and found to give a large number of well-marked bands, each of which represents a group of β rays, all of which are expelled with identical speed. It was at first thought that most of the energy of the β rays was comprised in these groups, as some of the bands on the photographic plate were very marked. Chadwick, however, has recently shown that the fraction of the rays which give a line spectrum is only a few per cent. of the total radiation. The general evidence shows that the β radiation from these substances gives a *continuous* spectrum due to β rays of all possible velocities, on which is superimposed a *line* spectrum due to a small number of β particles of definite velocity comprising each group.

Lines in the β-ray spectrum have been observed for particles which have a velocity not far from that of light, but the photographic effect of the particles becomes relatively feeble for such high speeds.

It is known from direct measurement that each atom of radium B or of radium C in its disintegration emits *on an average* one β particle. In the β-ray spectrum of radium C at least fifty definite bands are observed, differing widely in intensity. It is thus clear that a single atom in disintegrating cannot provide one β particle for *each* of these numerous groups. It is thus necessary to conclude that each atom does not emit an identical β radiation. The results are best explained by supposing that the β-ray spectrum is the statistical effect due to a large-number of atoms, each of which may only give one or two of the groups in its disintegration. In this respect a β-ray transformation is distinguished from an α-ray transformation, for in the latter case each atom emits one α particle of characteristic speed. It will be seen later that there is undoubtedly a very close connection between the emission of β and γ rays from radio-active atoms, and the probable explanation of the remarkably complex β-ray spectrum will be discussed later.

With the exception of one element, radium E, and possibly uranium X, all the radio-active substances which emit primary β rays give a line spectrum. For the majority of elements the strong lines in the β-ray spectrum have been determined by Baeyer, Hahn, and Meitner, but more intense sources of radiation will be necessary to map accurately the weaker lines.

γ RAYS.

The earlier experiments on the γ rays were mainly confined to a determination of the absorption of the more penetrating radiations

by different kinds of matter. It was early observed, however, that some of the radiations appeared to be complex. This was shown by anomalies in the initial part of the absorption curve. In the meantime, a notable advance in our knowledge of X-rays had been made by the work of Barkla. He found that under certain conditions each element when bombarded by X-rays of suitable penetrating power gave rise to a strong radiation which was characteristic for that element, e.g., the lighter elements from aluminium to silver emitted characteristic radiations called the " K " series, which increased rapidly in penetrating power with the atomic weight of the radiator. It was found that the heavier elements emitted in addition another characteristic radiation of softer type, which was called the " L " series. These results showed clearly that there must be definite structures within the atom which gave rise to a definite radiation under suitable conditions of excitation. From these results it seemed probable that the γ rays from radio-active matter must consist of the characteristic radiations of these heavy elements, analogous in type to the corresponding radiations observed in ordinary elements when excited by X-rays or kathode rays. These conclusions were confirmed by a series of investigations made by Rutherford and Richardson. The γ rays were analysed by means of their absorption by aluminium and by lead, the disturbing effects of the primary β rays being eliminated by means of a strong magnetic field. It was found, for example, that the γ rays from radium B, when examined by their absorption in aluminium, consisted of at least two types, one easily absorbed, and the other eighty times more penetrating. By further observations of the absorption of the γ rays by lead, Richardson found that the rays from radium B could be divided into at least four definite types, each of which was absorbed exponentially by lead. Similar results were obtained for all the radio active elements which emitted γ rays. In some cases the soft γ rays, e.g., those from radium B, corresponded to the characteristic radiation of the " L " series, and others to the " K " series. The general results, however, indicated that several additional series of characteristic radiations are present in some cases. It was clear from these experiments that the γ rays corresponded to the natural modes of vibration of the inner structure of the radio-active atoms. In the meantime the experiments of W. H. Bragg and W. L. Bragg, and of Moseley and Darwin, had shown that the characteristic X-radiations of the elements gave definite and well-marked line spectra. These spectra were simply determined by reflecting the rays from crystals. If this were the case, it seemed probable that the γ rays from the radio-active atoms would also give line spectra, and thus allow the natural frequencies of vibration of these atoms to be determined. During the past year, a number of experiments have been made to test this point by Rutherford and Andrade, using radium B and radium C as the source of γ radiation.

As was anticipated, it was found that the γ rays from radium B and radium C gave well-marked line spectra. The general method employed was to use an α-ray tube containing a large quantity of emanation as a source of radiation. The γ rays were reflected from a crystal of rock-salt, and the position of the spectrum lines determined photographically. Usually twenty-four hours were necessary to obtain a marked photographic effect. Special difficulties arose in these experiments which are absent in an investigation of a similar kind with X-rays. In addition to γ rays, the radio-active matter emits very penetrating β rays which have a strong photographic action; while the γ rays in their passage through matter themselves give rise, to high-speed β rays. The disturbing effect of these radiations has to be eliminated by placing the whole apparatus between the poles of a powerful electromagnet. In this way it was found that the spectrum of radium B consisted of a large number of lines, of which the most intense were deflected at angles of 1° 46', 10°, and 12°. The more penetrating radiation from radium C gave a strong line of 1° and a fainter line at 43'. The strong lines at 10° and 12° are due to easily absorbed γ rays, and undoubtedly correspond to the "L" radiation of radium B. The line at 1° corresponds to a very penetrating radiation which has a wave-length less than one-tenth of an Angström unit. The penetrating γ rays from radium C have by far the shortest wave-length so far observed. It does not seem probable that such short waves can be produced artificially in an X-ray tube unless possibly an exceedingly high voltage be applied.

There is one interesting result of these investigations that should be mentioned. The two strong lines of the radium B spectrum deflected at 10° and 12° were found to correspond exactly in position to the X-ray spectrum of lead. These experiments thus confirmed the view based on chemical evidence that radium B and lead were isotopic, *i.e.*, they were elements of practically identical chemical and physical properties, although their atomic weight differed by seven units.

CONNECTION BETWEEN β AND γ RAYS.

Before considering in detail the difficult problem of the connection between β and γ rays, it is desirable to summarise the main facts that have been established in regard to the relations between kathode rays and X-rays :—

(1) A small part of the energy of kathode rays falling on a radiator is converted into X-rays, the average frequency of the latter increasing with the velocity of the kathode particle.

(2) X-rays in passing through matter give rise to a β radiation. The initial energy of the escape of the electrons increases with the frequency, and is probably proportional to it.

(3) Electrons or X-rays of appropriate energy are equally able to excite the characteristic radiations in an atom.

The results which have been shown to hold for the X-rays hold equally for the β and γ rays, which have much greater individual energies, e.g., Gray and Richardson have shown that the β rays from radio-active matter are able to excite the characteristic radiations of the elements in a number of substances, while γ rays in passing through matter give rise to high-speed electrons. It was long ago suggested by Bragg that β rays and X-rays are mutually convertible forms of energy, e.g., a β particle falling on matter may be converted into an X-ray of the same energy, and the latter in passing through matter may in turn be converted into an electron of identical energy. This assumes that the energy of an X-ray and an electron are mutually convertible, and the energy may appear under suitable conditions in either of the two forms. While the general evidence indicates that this point of view may hold closely for the conversion of the energy of a single X-ray into that of a swift electron, it is very doubtful whether it holds for the converse case of the excitation of an X-ray by an electron. We shall see later from experimental evidence that in general the energy of the electron required to excite an X-ray of definite frequency is always greater than the corresponding energy carried off in the form of an X-ray.

It was early observed that there appeared to be a close connection between the emission of β and γ rays from radio-active matter. In all cases, the two types of radiation appeared together. A closer examination, however, showed that there were very marked differences between the relative energies of the β and γ rays from different radio-active elements. For example, radium C emits intense β rays and also intense γ rays; on the other hand, radium E emits intense β rays over a wide range of velocity, but exceedingly weak γ rays. Differences of a similar kind were observed amongst a number of the radio-active elements. One striking distinction, however, was to be noted. All the radio-active substances which give a marked line spectrum of β rays also emitted intense γ rays. On the other hand, a substance like radium E, which gave scarcely any γ rays at all, gave a continuous spectrum of β rays in which no lines have so far been observed. It thus appeared probable that the line spectrum of the β rays was intimately connected with the emission of γ rays, and this conclusion has been completely established by recent experiments. As we have seen, γ rays in passing through matter give rise to high-speed β rays. Using radium B and radium C as a source of γ rays, the β radiation excited in a number of metals by the passage of γ rays was analysed in a magnetic field by Messrs. Robinson and Rawlinson and the writer, and was found to consist in part of definite groups of β rays. When lead was the absorbing material, the magnetic spectrum of the β rays excited by the γ rays was found to be nearly identical with the primary β-ray spectrum

of radium B. This striking result shows that those β rays escaping from the radio-active atom which give rise to a line spectrum must result from the conversion of γ rays into β rays in the radio-active atom. The slight differences observed in the spectrum for different metals is probably connected with the enegy required to excite one of the characteristic radiations of the element used as absorber.

An explanation of the marked differences in the character of the β and γ radiation from different radio-active atoms can, I think, be given on the following lines. Some of the γ rays are broken up in their escape from the atoms, and the energy of each converted γ ray is transferred to an electron which escapes with a definite velocity dependent on the frequency of the γ radiation. Taking into account a large collection of disintegrating atoms, each of the possible modes of characteristic vibration of the atom gives rise to an electron of definite speed. In this general way we may account for the line spectrum of the β rays which is so commonly observed. On this view, we should expect to obtain a well-marked line spectrum of β rays when a substance emits strong γ rays—a result in accord with observation.

In order to account for the marked differences in the types and intensity of γ rays from different radio-active substances, it seems necessary to suppose in addition that the primary β particle always escapes from the nucleus in a *fixed* direction with regard to the structure of the atoms under consideration. For example, we have already pointed out that radium E, although it emits intense β rays which give a continuous spectrum over a wide range of velocity, emits very weak γ rays. Since there can be no doubt that the β rays have sufficient speed to excite the characteristic modes of vibration which must be present in the atom, we are driven to the conclusion that the β particle escapes in such a direction that it does not pass through these vibrating centres. On this view, the type of characteristic γ rays which are excited, and consequently also the corresponding speed of the β rays which arise from the converted γ rays, will depend entirely on the direction of escape of the primary β particle. The definite direction of escape of the primary β particle, which varies for atoms of different substances, also suffices to explain a number of other differences observed in the mode of release of energy from various radio-active atoms. It is supported by many other observations which indicate that the atoms of a particular radio-active substance break up in an identical fashion.

We have so far considered only in a qualitative way the relation between the groups of rays in a β-ray spectrum and the emission of characteristic γ rays. During the last few years there has been a growing body of evidence that the energy E carried off in an X-ray of frequency ν is proportional to this frequency, and is given by $E = h\nu$ where h is Planck's fundamental constant. If the whole of the energy of an X-ray can be given directly to an electron, the

energy communicated to the latter should be $h\nu$. There is no doubt that in many cases this simple relation holds very approximately, but the measurements so far available are not sufficiently precise to settle definitely whether a part of the energy may not appear in another form.

Assuming that the transfer of the energy from an X-ray to an electron is complete, we should expect to find groups of β rays of energy corresponding to $h\nu$ where ν is the frequency of the γ rays found experimentally. Such a relation is found to hold within the limit of experimental error for three marked groups of low-velocity β rays emitted from radium B. On the other hand, it is found that many of the high velocity groups of β rays both from radium B and radium C have energies many times greater than correspond to any observed frequency. Not the slightest evidence, however, has been obtained that the corresponding high frequencies of vibration exist in the radio-active atom; in fact, all the evidence points to the fact that these high-speed electrons arise from one or more of the observed frequencies in the γ-ray spectrum.

In order to account for such results, it seems necessary to suppose that the γ rays of high frequency are not necessarily emitted as single pulses, but consist of a train of pulses either produced simultaneously or following one another at very short intervals. Each of these pulses has an energy $h\nu$ corresponding to the frequency ν, but the total energy in the train of waves is $ph\nu$ where p is a whole number, which may have possible integral values 0, 1, 2, 3, . . . etc., depending on the structure of the atom and the conditions of excitation. The penetrating power of such a train of waves corresponds to that of a single wave of frequency ν, but on passing through matter the energy of the whole train of p waves occasionally may be transferred to an electron which consequently is expelled with an energy $ph\nu$. There is very strong evidence of the general correctness of this point of view, for most of the stronger lines in the β-ray spectrum of radium C have energies which correspond to an *integral* multiple of the energy corresponding to the strong lines actually observed in the γ-ray spectrum. It seems probable that under the ordinary conditions of excitation by kathode rays in a vacuum tube, the X-ray contains only one pulse or wave, but under the far more powerful stimulus of the very swift β particle escaping from the atom, a long train of waves, each of the same frequency, is produced. The energy of the whole train of waves may under suitable conditions be given to an electron, which consequently has a speed very much greater than that impressed upon it by a single wave of the same frequency.

Limit to the Frequency of Vibration of the Atom.

There is one question of fundamental importance which arises in considering the modes of vibration of the atom, viz. whether there

is a definite limit to the frequency of the radiation which can be excited in a given atom. Theory does not provide us with an answer to this problem, since little is known about the conditions of excitation, nor even of the nature of such high-frequency vibrations. A study of the frequency of the γ rays from radio-active substances is of great importance, as it throws much light on this problem.

As we have seen, the energy of the β particle escaping from the nucleus of radium C is equivalent to that acquired by an electron moving in an exhausted space under a potential difference of several million volts. This high-speed electron passes through the electronic distribution in its escape from the atom. Notwithstanding such ideal conditions for the excitation of high-frequency radiations of the atom, the highest frequency in the radiation emitted by radium C is only about twice that obtainable from an ordinary hard X-ray tube excited by 100,000 volts. It thus appears probable that there is a definite limit to the frequency of the radiation obtainable from a given atom, however high the speed of the disturbing electron. This limiting frequency is determined not by the speed of the electron but by the actual structure of the atom. Since the γ radiation from radium C gives a line spectrum, it would appear that the highest frequency obtainable is due to a definite system of electrons which is set into characteristic vibration by the escape of a β particle. In order to throw further light on this point, Prof. Barnes, Mr. H. Richardson and myself have recently made experiments to determine the maximum frequency obtainable from an X-ray tube for different constant voltages. The Coolidge tube, which has recently been put on the market, is ideal for this purpose, as it provides powerful radiation at any desired voltage. The anti-kathode is of tungsten of atomic weight 184, so that we are dealing in this case with the possible modes·of vibration of a heavy atom. The maximum frequency of the radiation was deduced by measuring the absorption by aluminium of the most penetrating rays emitted at different voltages. The absorption of X-rays of different frequencies by aluminium has been examined over a very wide range, and can be expressed by simple formula. It was found that for 20,000 volts the frequency of the radiation was slightly lower than that to be expected if Planck's relation held. With increasing voltage there is a rapid departure from Planck's relation. The frequency reaches a maximum at about 145,000 volts, and no increase was observable up to the maximum voltage employed, viz. 175,000 volts. The experiments thus show that the frequency of radiation reaches a definite maximum. which is no doubt dependent on the atomic weight of the particular radiator employed. It is of interest to note that the maximum penetrating power of the X-rays from the Coolidge tube in aluminium is about the same as the γ rays from radium B, but is about three-tenths of the γ rays from radium C. There is evidence which suggests that the very penetrating γ rays from radium C correspond to the octave

of the " K " characteristic radiation of that element.   If this be the case, it may prove possible that a still more penetrating radiation might be obtained from tungsten, but in order to excite it a voltage of the order of a million volts would probably be required.   In any case, it seems clear that Planck's relation does not hold for excitation of high frequencies by swift electrons, but may hold very approximately for lower frequencies corresponding to the radiation excited by a few hundreds or thousands of volts.   On the other hand, the evidence obtained from a study of the β rays excited by X-rays or γ rays certainly indicates that the relation $E = ph\nu$ holds at any rate very approximately for the highest frequency examined.   It is thus obvious that the emission of β and γ rays from the radio-active atoms is clearly connected with the general theory of radiation, and it seems likely that a close study of these radiations will throw much light on the mechanism of radiation in general.

There can be little doubt that the penetrating γ rays from active matter have their origin in the vibration of electronic systems in the structure of the atom outside the nucleus.   The nucleus itself, however, must be . : lently disturbed by the expulsion of an α or β particle.   If this leads to the emission of a γ radiation, it must be of exceedingly high frequency, as the forces holding together the component parts of the nucleus must be exceedingly intense.   We should anticipate that this radiation would be extraordinarily penetrating, and difficult to detect by electrical methods.   So far no experimental evidence has been obtained of the existence of such very high-frequency radiations, but it may be necessary to devise special methods before we can hope to do so.

[E. R.]

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